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SUPERCRITICAL FLUIDS: NANOTECHNOLOGY AND SELECT EMERGING APPLICATIONS

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SUPERCRITICAL FLUIDS: NANOTECHNOLOGY AND SELECT EMERGING APPLICATIONS

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In this paper, a selected list of emerging applications of supercritical fluids (SCFs) are presented. In particular, demonstrated facts for the promise of the nanoscale science and technology and its overlap or interface with the SCFs technology are presented. It is argued that nanoengineered materials at the nanoscale have mechanical, optical, chemical, and electrical properties quite different from the bulk material. Examples of enhanced performance of many such materials when they are used in practical applications are given. SCFs, in particular carbon dioxide, on account of their special properties such as zero surface tension, low viscosity, and high solubility, enable them to play a critical role in many advanced technology applications. For example, as miniaturization efforts approach the nanoscale, surface tension forces become an important factor in many nanotechnology processes such as lithography in the electronic industry. In particular, the zero-surface-tension property of the SCFs presents them as a natural choice for nanotechnology

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processes. Cases are presented where SCF technology could enhance the advancement of nanotechnology or when the two technologies could have synergistic contributions to the synthesis and design of new materials and possibilities are presented. For example, advances in nanoscience and supercritical fluids have contributed to a better design and understanding of the composition, size, and structure of catalysts, crystals, sol-gels, and composite material performance.

Keywords: supercritical, nanotechnology, nanoparticle, nanotube, SWCNT, MWCNT, RESS, sol-gel, solvent, nano-catalyst, aerogel, mizelle, polymer foam, nano-composite, microemulsion, antisolvent, cryogenic rocket engine

INTRODUCTION

In the past 15 years, supercritical fluid extraction technology has attracted considerable attention from researchers for its potential applications as an environmentally friendly solvent for chemical processing, see Kiran and Levelt Sengers (1994) and McHugh and Krukons (1994a, 1994b). Supercritical fluids exhibit liquid-like solvation capabilities and gas-like mass and momentum transfer properties. Because of their high diffusivities, SCFs are capable of penetrating into porous solid materials dissolving organic compounds. Because of their low viscosities, SCFs can be transferred in pipelines and pumped to high pressures requiring less mechanical energy than liquids and subcritical gases.

Because the density of an SCF can be altered continuously by manipulating pressure and temperature, the solvation ability of the fluid is tunable. Thus, selective dissolution of solutes in a SCF may be achieved by optimizing the density of the fluid phase. This tunable solvation characteristic is a unique property that makes SCFs different from conventional liquid solvents. The other important advantage of SCF extraction is rapid separation of solutes that can be easily achieved by a reduction of pressure. Examples of large-scale commercial applications of the supercritical fluid extraction technology include crystallization, Hu and Lesser (2004), extraction of vitamins, natural flavors, perfumes, and essential oils from fruits and plants, Mansoori et al. (1988) and Martinelli et al. (1991), removal of unwanted materials, such as caffeine and cholesterol from food products, Mohamad and Mansoori (2002), and pollution remediation using environmentally friendly supercritical fluids Ekhtera et al. (1997).

The objectives of this paper are to bring to the attention of the scientific community opportunities for multidisciplinary research using SCFs, in particular, those that exist at the interface of SCF technology and nanotechnology due to their intrinsic overlap. The natural blending of supercritical fluids and nanotechnology will be made clear in this article. It is also the author's intention to stimulate further investigations into applications of SCFs. This paper is not meant to be a comprehensive review and analysis of the current state of the art in SCF technology, but rather a concise overview of some selected current and emerging applications.

In what follows, the historical birth and importance of nanoscience are described followed by a concise presentation to understand special properties of SCFs. Then, examples on selected applications of SCFs in areas of propulsion, green chemistry, lithography, and materials are given. Later, close attention is paid on the application and synthesis of nanoparticles due to their importance in nano-science and technology as building blocks. Only nanoparticle manufacturing methods that employ special properties of the SFCs are presented here. Next, the important role of SCFs in polymer industry is magnified. A few emerging applications at the interface of the SCF and nanotechnology are described. This paper ends with future trends, summary and conclusions.

NANOSCIENCE AND TECHNOLOGY (SIGNIFICANCE, CLASSIFICATION, AND APPLICATIONS)

Although scientists have long been working with "nano" sized entities, the historic birth of nanotechnology is commonly considered when Richard P. Feynman, the famous Nobel Laureate physicist, delivered his landmark lecture entitled, "There's Plenty of Room At The Bottom—An invitation to enter a new field of physics" on December 29, 1959, at the California Institute of Technology, see Feynman (1959). Feynman stated in his lecture that the entire encyclopedia of Britannica could be put on the tip of a needle and, in principle, there is no law preventing such an undertaking. He then challenged the scientific community and set a monetary reward to demonstrate experiments in support of such a miniaturization. This challenge was met by a team of Northwestern University researchers using a nanotech tool called the Atomic Force Microscope (AFM).

The term "nano" refers to a reduction of size, or time, by 10^{-9} . A nanometer is 10^{-9} meter. A human hair diameter is about 50 microns

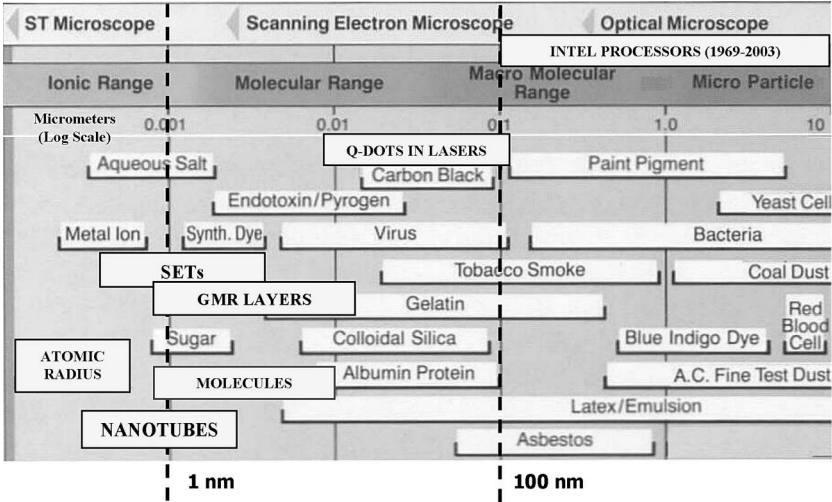


Figure 1. Shows size ranges for many entities as compared to selected nanotechnology products: SET (single-electron transistor), GMR (Giant magneto resistive), Q-DOTS (Quantum dots).

(i.e., 50×10^{-6} meter) in size, meaning that a 50 nanometer object is about 1/1000th of the thickness of a hair. Figure 1 shows size ranges for various submicron objects starting with ions, atoms and molecules. Size ranges of a few nanotechnology objects (like nanotube and quantum dot diameters) are also shown in this figure. It should then be obvious that nanotechnology, nanoscience, and nanoengineering deal with world much smaller in size than everyday human experience. Officially, the National Science Foundation defines nanoscience/nanotechnology as studies that deal with materials and systems having the following key properties. (1) Dimension: at least one dimension from 1 to 100 nanometers (nm). (2) Process: designed with methodologies that show fundamental control over the physical and chemical attributes of molecular-scale structures. (3) Building block property: they can be combined to form larger structures. Nanoscience, in a general sense, is quite natural in microbiological sciences considering that the sizes of many bioparticles (like enzymes, viruses, etc.) fall within the nanometer range.

Figure 2 shows some of the important present and expected future products and possibilities resulting from advances in nanotechnology. This figure indicates the broad list of applications and impact of

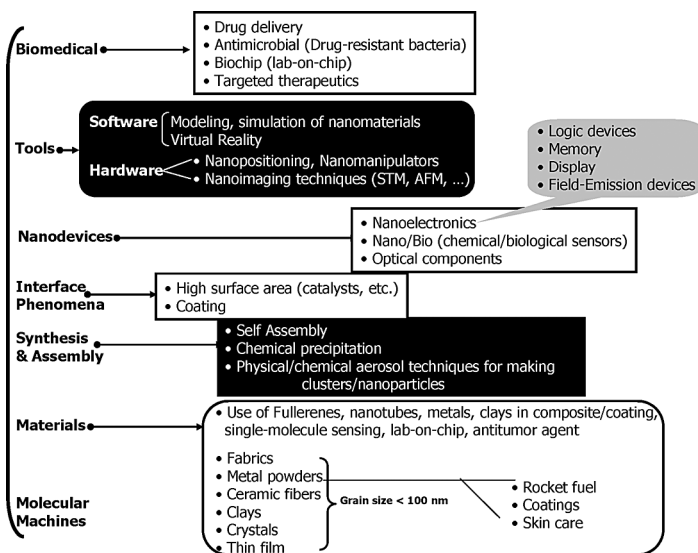


Figure 2. Shows the impact of the nanoscience in a number of technologically important areas. Courtesy of Nanoanalytic Group, Chehroudi et al. (2002).

nanotechnology. This list is rapidly growing and the effects are being felt in increasingly broader areas, with nanoelectronic, nanolithography and drug delivery industries presenting a tight focus and immediate interest. Figure 3 shows the expected trend in lithography advances indicating various technologies under investigation for development of pilot and production lines of integrated circuits (IC), see ITRS (1999). As an example, the half pitch of the DRAM (i.e., smallest feature size) is expected to go below the 100 nm mark by about 2005. Adverse economical factors could obviously delay the pace of development and hence affect the milestone dates predicted in Figure 3. Currently, the pursuit of mass-produced and inexpensive miniaturization processes by the semiconductor industry has reduced the line widths on IC chips down to about 100 nm via extension of the standard photolithography, see Takashi and Shinji (2000). Considering that the wavelength of the laser light source determines the width of the smallest line that could be formed on a wafer, to pattern ever-finer lines by the use of photolithography, the industry is now making a transition from krypton-fluoride (KrF) excimer laser light sources (248 nm) to argon-fluoride (ArF) lasers emitting at 193 nm. Within a few years, even ArF wavelength

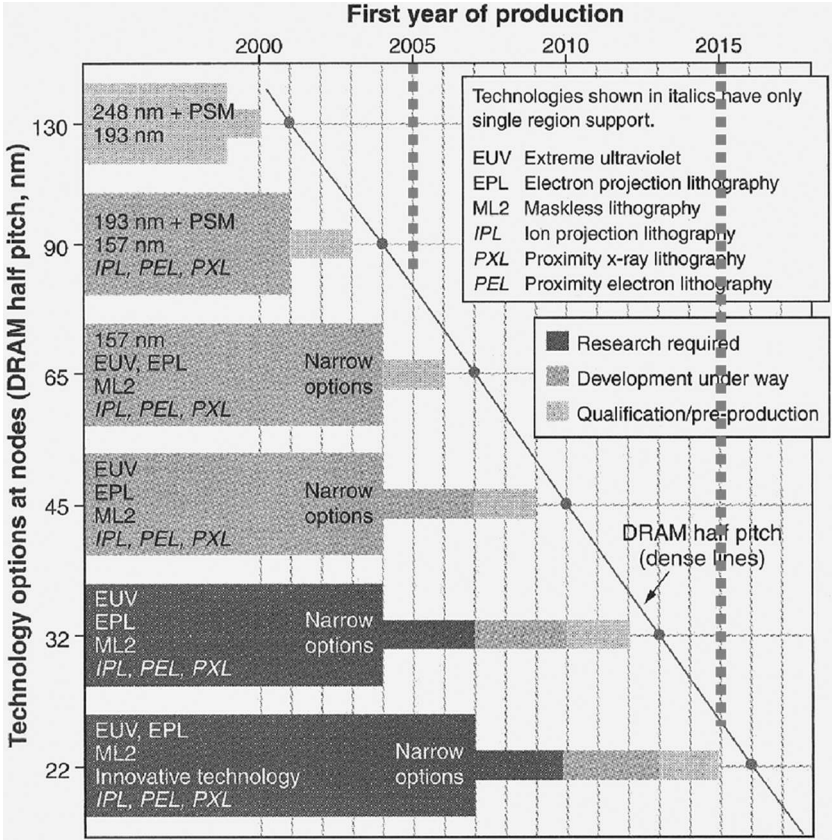


Figure 3. International technology roadmap for semiconductors (ed. International SEMATECH) (<http://www.itrs.net/> (1999)).

will be too long and Fluorine (F_2) lasers at 157 nm will be needed. This would create serious material challenges, as most common optical materials do not transmit at this wavelength. Beyond the F_2 laser lies the transition to extreme ultraviolet (EUV), or “soft” X-rays, at 13 nm (see Figure 3). In nanotechnology, this method of fabrication (i.e., photolithography) is referred to as a “top-down” approach. The standard microelectronic fabrication for inexpensive and mass-produced integrated circuit chips could reach its limit and then enters into the nanofabrication territory, something not yet converged and subject of intense research.

The essence of the “nano-” science and technology is based on the finding that properties of matter in this size range differ from those of bulk material. For example, particles ranging in size from roughly 1 to 50 nm exhibit physical, chemical, optical, magnetic, and other properties that are intermediate between those of the smallest element from which they can be composed (such as a metal atom) and those of the bulk material. By far the most popular products in nanotechnology are the Buckminsterfullerene molecules (or Fullerenes, C_{60}) and carbon nanotubes with their peculiar properties. Carbon nanotube was first discovered in 1991 by Sumio Iijima, using an electron microscope while studying cathodic material deposition in an arc-evaporation reactor during the synthesis of Fullerenes, see Iijima (1991). The structure of this newly discovered material consisted of graphene cylinders that were closed at either ends with caps containing pentagonal carbon rings. The cylinder diameter range (from 1 to a few nanometers) was much smaller than the cylinder length range (from 1 to a few micrometers). A variety of other manufacturing schemes has since been developed to synthesize and purify carbon nanotubes with tailored compositions and structural functionalities. For example, practitioners now routinely use the techniques of laser ablation, chemical vapor deposition and metal-catalyzed disproportionation of suitable carbonaceous feedstocks to tailor their nano- synthesis, see Dai (2001) and Mickelson et al. (1999). Nanophased materials, so called because of the intrinsic size of their building blocks, have been shown to exhibit unusual photochemical, electronic, thermal and mechanical properties never seen before in their corresponding bulk counterparts or anticipated from conventional understanding at the molecular level, see Dresselhaus et al. (1996) and Ruoff and Lorents (1995).

This is because such particles can behave as isolated quantum states. For example, depending on their chirality and diameter, single-walled carbon nanotubs (SWCNTs) could behave as metallic, semimetallic, or semiconductive one-dimensional objects (Dresselhaus et al. (1996)), and their longitudinal thermal conductivity could exceed the in-plane thermal conductivity of graphite, see Ruoff and Lorents (1995). Very high tensile strengths (~ 100 times that of steel) of ropes made of SWCNTs has recently been determined experimentally, see Yu et al. (2000). When dispersed in another medium, SWCNTs could retain their intrinsic mechanical attributes or even augment the structural properties of their medium host, see Andrews et al. (1999). SWCNTs have the

electrical conductivity of copper, thermal conductivity of diamond, and the highest strength, toughness, and stiffness when compared to any other known molecule.

An important application of nanotechnology would be the production of nanocatalysts. A catalyst performance is sensitive to its particle size because the surface structure and electronic properties could change greatly due to size changes. For example, the heat of adsorption for CO and the activation energy for CO dissociation, both, change with decreasing the size of Ni catalyst particles, a pattern that affects the performance of Ni nanoparticles in the Fischer–Tropsch synthesis of hydrocarbons from synthesis gas (a mixture of CO and H₂), see Bell (2003). Considering that nearly one-third of the material gross national product in the United States involves a catalytic process somewhere in the production chain, the impact of only this one application of nanotechnology could be immensely felt. In fact, the U.S. government forecasts that in just another 10 to 15 years, nanotechnology will impact more than \$1 trillion per year in products and services. And, with the passage of the 21st Century Nanotechnology Research and Development Act the U.S. government will be spending almost \$4 billion dollars for fiscal years of 2005–2008 through the National Nanotechnology Initiative (NNI), one of the President's highest multi-agency research and development priorities.

Finally, due to their size range overlap, applications of the nanoscience and nanotechnology in biological areas, cancer treatment, drug delivery, and many others are rapidly increasing. Nobel Laureate, Richard E. Smalley, commenting on the importance of nanotechnology said: "It holds the answer, to the extent there are answers, to most of our most pressing material needs in energy, health, communication, transportation, food, water, etc."

WHAT IS A SUPERCRITICAL FLUID?

For a pure material, a supercritical fluid (SCF) is defined as a substance that exists above its critical temperature, pressure and density, see Sun et al. (2001) and Poliakoff and King (2001). However, it is also loosely defined as a solvent above its critical temperature because under these conditions the solvent exists as a single phase regardless of its pressure, see Sun et al (2001). Figure 4 shows the phase equilibrium diagram of a pure substance (water) indicating the critical point (CP) and the two-phase region. As a pure substance approaches its CP, drastic changes

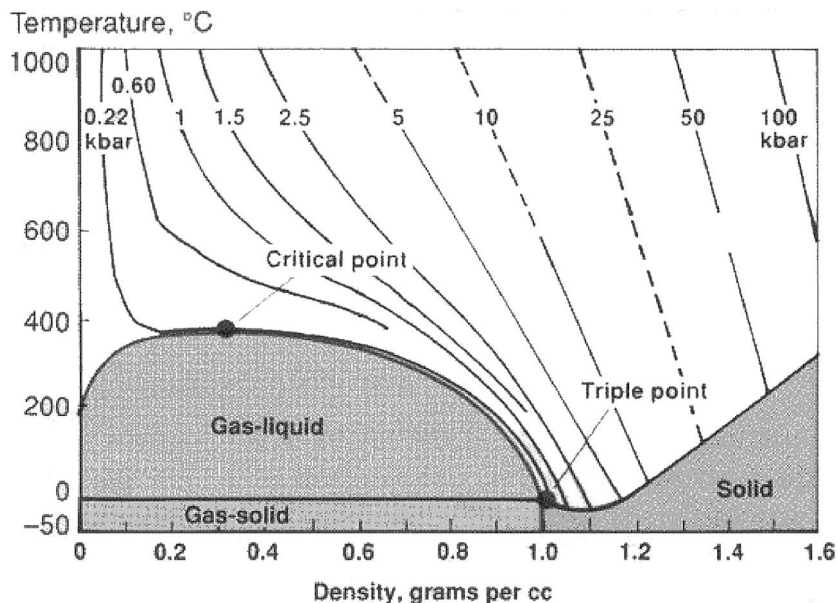


Figure 4. Phase diagram for water indicating critical point and two-phase equilibrium regions. Shaw et al. (1991).

in some important thermophysical properties are observed. For example, a sharp distinction between the liquid and gas phases disappears at and above the CP, and the substance is more properly considered as a fluid. We no longer have surface tension and the heat of vaporization becomes zero under supercritical conditions.

The densities of SCFs are like liquids and highly dependent on the pressure when they are near their critical points. The fluid density can vary or be “tuned” between those shown by gases to those at liquid-like values. This property is especially important for synthetic applications, in which reaction conditions (e.g., selectivity, rates, pathways) may be sensitively manipulated by pressure variations. Such a reaction control is impossible using traditional organic liquid solvents. Diffusivity and viscosity of a SCF are gas-like, and hence exhibit high mass transfer and low momentum transfer rates. Solubility of various compounds in SCFs depends on many factors, some of which are their densities, polarities, molecular interactions, and hydrogen bonding. As far as the SCF density is concerned, higher SCF density correlates with higher solubility

of solutes in that SCF at a given temperature. However, when the temperature is increased at constant pressure, the SCF solvent density is reduced and hence the solute solubility is lowered. However, vapor pressure of the solute increases with temperature.

It is interesting to point out that near the CP, most of the anomalies in the thermodynamic and transport properties (for example, see Figure 5) can be set in a form of scaled, universal power law functions with respect to the critical point parameters, see Seibert et al. (2001). This has a very important consequence that any results obtained with one fluid can be immediately rescaled to describe any member of a whole class of systems, called a "class of universality." For example, the specific heat at constant volume, C_v , although very large at the CP, is proportional to $\varepsilon^{-\alpha}$ ($\alpha = 0.1105 + 0.025/-0.027$) near the critical point. The exponent is universal and its precise determination was a key test of the Renormalization Group theory developed to improve the classical macroscopic description of fluid behavior close to the critical point.

In many applications, one must deal with issues specific to the mixture of pure substances. For mixtures, we no longer have a single critical point and determination of critical conditions (called the "critical mixing

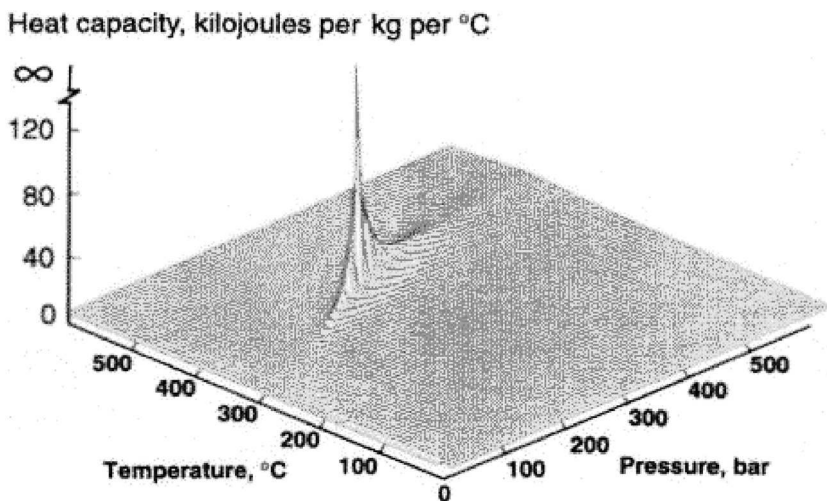


Figure 5. Behavior of heat capacity as a function temperature and pressure near the critical point of water (Critical pressure and temperature values are 221 bar and 374°C). Shaw et al. (1991).

temperature or pressure”) can be a complex task, see Bruno and Ely (1991). For example, critical curves are seen for two-component mixtures as opposed to a critical point for a pure substance. As an example, consider a pure hydrocarbon drop in a nitrogen environment. It is found that the amount of nitrogen dissolved in a thin layer of the surface of the liquid drop increases with pressure, see Umemura (1994). As a result, the critical mixing temperature of the layer decreases, Lazar and Faeth (1971). This layer of nitrogen and hydrocarbon mixture spreads spatially in time. More details on critical conditions for mixtures can be found in McHugh and Krukoniš (1994a).

Another interesting aspect of these fluids is that local density effects exist in supercritical fluid solutions specially near the critical point. It is shown that although SCFs may be considered macroscopically homogeneous (remaining one phase regardless of the pressure), microscopic inhomogeneities (specially near the CP), consisting of clusters of solvent molecules and free volumes, do exist. For example, solvent–solute clustering, defined as a locally higher-than-the-bulk solvent density about a solute molecule, is observed. Enhanced solvation in supercritical CO₂ is thought to result from clustering of the solvent around the solute, and this clustering will also influence chemical reactivity. Interestingly, for different SCFs, a common pattern exists for density dependence of this solute-solvent interaction. This common pattern is usually characterized by observation of three different responses (spectroscopic or other responses) in three density regions: (1) a rapid increase in the response in the low-density region; (2) a plateau-like response in the near-critical zone; and (3) a further increase in response in the high-density region. For more details see Sun (2002).

In addition to the solvent-solute interaction mentioned above, solute-solute clustering, defined loosely as local solute concentrations that are greater than the bulk solute concentration, are also observed. An important result of this effect is the enhancement of bimolecular reactions in supercritical fluid solutions. In a related subject, it is found that a small addition of a polar cosolvent could dramatically improve the solubility of organic analytes in a supercritical fluid. Furthermore, this addition causes solubility enhancements that is solute-specific, with more dramatic solubility increases for polar solutes. In a sense, solutes in SCF-cosolvent mixtures are mostly surrounded preferentially by the cosolvent molecules, a kind of solute-solute clustering, see Sun (2002).

SELECTED EMERGING APPLICATIONS OF SCFs

Propulsion

Although there are other applications of SCFs in propulsion related areas (some of which are presented later in this paper), key findings from the studies conducted and directed by the author in the past five years are summarized in this section. In a design of a chemical rocket engine, liquid fuel and oxidizer are often injected as round jets (for instance, coaxial or impinging jet types), into a hot and elevated-pressure environment of the thrust chamber. Higher specific impulse is a major motivation for operating rocket thrust (or combustion) chambers at progressively higher pressures. Consequently, as the combustion chambers are designed to operate at higher pressures, conditions may exist in which an injected liquid finds itself near or even above the thermodynamic critical condition. Examples are the Space Shuttle main engine and Vulcain (Ariane 5) engine which are fueled with liquid H_2 and liquid O_2 .

More information was needed on liquid jets injected into supercritical condition when this author began working on SCFs. During the past 10 years, investigators around the world have conducted intensive numerical and experimental research studies to understand the behavior of the liquid jets (single or coaxial) injected into a supercritical ambient conditions, for example see Mayer et al. (1998), Bellan (2000), Oefelein and Yang (1996), and Umemura and Wakashima (2002). Chehroudi et al. (2000, 2002a and 2002b) reported extensive experimental results from the injection of several fluids at sufficiently high Reynolds numbers to ensure a fully-turbulent flow at the exit of the injector. A variety of ambient fluids are used into which pure liquid N_2 , He, and liquid O_2 fluids were injected. The effects of chamber pressure (density) ranging from sub- to supercritical pressures at a supercritical chamber temperature (based on the critical pressure and temperature, P_c , T_c , of the injectant) were observed by the acquisition of shadowgraph images from the injector exit region, see Figure 6.

It can be seen in Figure 6 that at sufficiently low subcritical chamber pressures, the disturbances on the jet interface were amplified downstream and eventually broke up into irregularly-shaped small entities. A further increase of chamber pressure initiated formation of many small ligaments and droplets at the interface of the jet only within a narrow regime below the critical pressure of the injected pure fluid, resembling a second wind-induced liquid jet breakup, see Reitz and Bracco

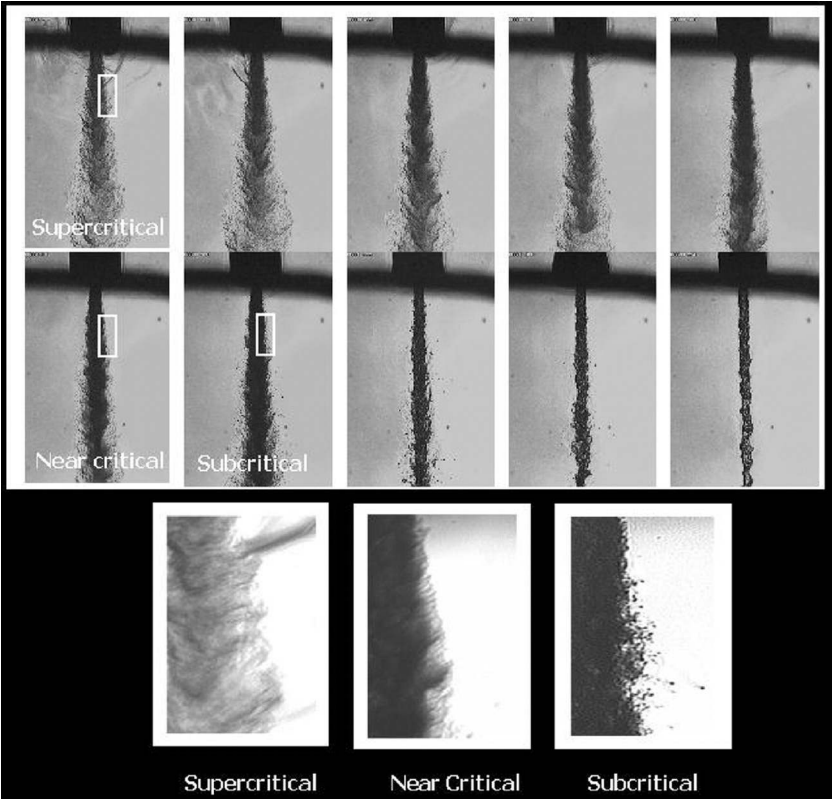


Figure 6. Back-illuminated images of cryogenic liquid nitrogen injected into a nitrogen at a fixed supercritical temperature of 300 K but varying sub- to supercritical pressures ($P_{\text{critical}} = 3.39 \text{ MPa}$; $T_c = 126.2 \text{ K}$). $P_{\text{ch}}/P_{\text{critical}} = 2.74, 2.44, 2.03, 1.62, 1.22, 1.03, 0.83, 0.62, 0.43, 0.23$; from upper left to lower right. $Re = 25,000$ to $75,000$. Injection velocity: $10\text{--}15 \text{ m/s}$. Fround number: $40,000$ to $110,000$. Injectant temperature: 99 to 120 K . Chehroudi et al. (2002a).

(1979). At even higher chamber pressures, near but below the critical pressure of the injectant, the expected transition into a full atomization regime to produce a liquid spray is inhibited due to reduction, and eventual elimination, of both the surface tension and the heat of vaporization. The jet appearance changes abruptly at this pressure and resembles that of a turbulent gas jet for all higher chamber pressures. The initial growth rate of the jet was plotted together (not shown here) with available data on liquid fuel injection in diesel engine environments, and turbulent

incompressible, supersonic, and variable-density jets and mixing layers. At near- and super-critical pressures, measurements by Chehroudi agreed well with the theoretical growth rate equations proposed by Brown (1974), Papamoschou and Roshko (1988), and Dimotakis (1986) for incompressible but variable-density turbulent mixing layers. This constituted the first quantitative evidence in support of the past qualitative observations that the jet appeared to evolve into a gas-like behavior under supercritical ambient condition.

The geometry of the jet interface was also examined for the first time by fractal analysis. The results clearly indicated a transition from a Euclidean to a fractal interface, with a fractal dimension close to the values measured for gaseous turbulent jets. This provided additional quantitative evidence for the hypothesis that the jets evolve into a gas-like behavior. In addition, an equation based on a proposed physical mechanism combined with the characteristic gasification time (τ_g) and interfacial "bulge" formation/separation time (τ_b) was proposed, $\theta = 0.27[(\tau_b/(\tau_b + \tau_g) + (\rho_g/\rho_l)^{0.5})]$, that showed good agreement with the measured initial growth rate (θ) data. It was found that the transition point from sub- (liquid-jet-like) to supercritical (gas-jet-like) behavior occurs when the time scale ratio ($\tau_b/(\tau_b + \tau_g)$) is approximately equal to 0.5. The proposed model equation by Chehroudi agreed well with the experimental growth rate data. Finally, the initial growth rate using results from Raman scattering was also in reasonably good agreement with measurements by shadowgraphy if twice the full-width half-maximum (FWHM) of the normalized Raman intensity radial profiles were used, see Chehroudi et al. (2000). Parallel computational studies by Okong'o et al. (2002), Zong and Yang (2003), and Barata et al. (2002) showed results consistent with the Chehroudi's findings.

Environmental Issues (Green Chemistry) and Solvent-Free Cleaning

Organic solvents are an important component of many industrial processes. Unfortunately, many of these solvents have adverse environmental and health effects. For these reasons, organic solvents such as halogenated hydrocarbons (e.g., chloroform and dichloromethane) are being phased out and benign replacements are being developed. In 1991, the U.S. Environmental Protection Agency (EPA) created a Green Chemistry Program within the Office of Pollution Prevention and Toxics

(OPPT) to support what is referred to as a "benign-by-design" approach in the design, manufacture, and use of chemicals and chemical processes. Green chemistry is an approach towards a sustainable industrial development, see Polikoff and Anastas (2001). The term "sustainable development" was defined in the 1987 United Nations report "Our Common Future," as development that meets the needs of the present without compromising the ability of the future generations to meet their needs. This program, in conjunction with the Pollution Prevention Act of 1990, focuses on source reduction of pollutants as opposed to industrial focus on waste management and pollution control. Also, the EPA's OPPT teamed up with the National Science Foundation (NSF) to fund worldwide green chemistry research. Much of the recent funding has been directed at research that exploits the unique properties of supercritical fluids as an alternative to traditional solvents. Furthermore, the Federal Resource Conservation and Recovery Act, intended to suppress soil, air, and water pollution, has initiated strict regulations regarding on-site storage, recycling and disposal, and off-site waste transport. Finally, green chemistry proponents have created 12 principles of the green chemistry, being one of the important steps towards its proper implementation, see Anastas and Warner (1998) for details. Green Chemistry Institute's director, Dennis L. Hjersen, states in CHEM-RAWN (Chemical Research Applied to World Needs) XIV conference "Much of green chemistry is focused on how we can bring biologists together with chemists, with engineers, with scientists from a range of disciplines because a lot of issues that we are dealing with now are so complex and so multidisciplinary that if we don't combine our forces we don't have a chance to solve them."

Considering the foregoing statement, it would be of tremendous value to have media that would serve as a versatile solvent without carcinogenic and environmental degradation effects. This objective has indeed been realized by the advent of supercritical fluid technology. Supercritical CO₂ and water are attractive alternatives because they are inexpensive and offer minimal threat to the environment or human health. Note that although CO₂ is considered as a greenhouse gas, it can be recovered and collected from sources such as industrial chemical processes and natural storages with little or no contribution to the greenhouse gases.

Many hazardous wastes materials, such as polychlorinated biphenyls and unused explosives, are organic compounds. These materials are usually insoluble in water and difficult to treat at ordinary temperatures

and pressures. However, most organic compounds readily dissolve in supercritical water and with an oxidizer (such as oxygen or hydrogen peroxide) many of them quickly react to produce mostly water and carbon dioxide. At high temperatures and pressures, above 200 bar, water is completely miscible with most hydrocarbons, including pentane, heptane, benzene, and toluene. Some hydrocarbons decompose and their dissociation reactions occur in the presence of supercritical water, even in the absence of air and other oxidizers. In the early 1970s scientists found that processing wood chips in a water reactor below the critical temperature produced tough tars. However, at temperatures above the critical temperature a much more complete reaction of the test materials was achieved (i.e., no tar and a clean reactor). Almost a decade after, James F. Welch at the National Bureau of Standards developed a reactor containing supercritical water and hydrogen peroxide that effectively destroyed a mixture that simulated torpedo fuel. At Modec Corp., Modell and coworkers demonstrated that municipal sewage sludge in a reactor containing supercritical water and oxygen could be transformed to an odorless, colorless aqueous solution (mostly water), odorless gases, and a small amount of solid inorganic residue, see Modell (1982) and Modell and Magdalena (2001). He also showed that pulp mill waste undergoes a similar transformation in supercritical water.

To better understand the process involved in such physio-chemical changes, researchers have been using spectroscopy to investigate the mechanisms of decomposition of organic compounds in supercritical water. Researchers at Los Alamos National Laboratory (LANL) used a variety of techniques, including laser spectroscopy, on samples in both batch and flow reactors to study the decomposition of rocket fuel and other propellants in supercritical water. Also, at Sandia National Laboratories, researchers studied with spectroscopic techniques the use of supercritical water for hazardous-waste destruction, mixed waste processing, and contaminated water cleanup, in optically accessible facilities.

Supercritical and liquid CO_2 , as solvents, are effective agents for both extraction-type cleaning that removes materials from within a substrate, such as fabric cleaning, and for surface-cleaning applications in manufacturing. Supercritical fluids are able to spread out along a surface more easily than a true liquid because they have lower surface tensions than liquids. At the same time, a supercritical fluid maintains a liquid's ability to dissolve substances that are soluble in the compound, which a gas cannot do. In the case of supercritical CO_2 , this means oils and

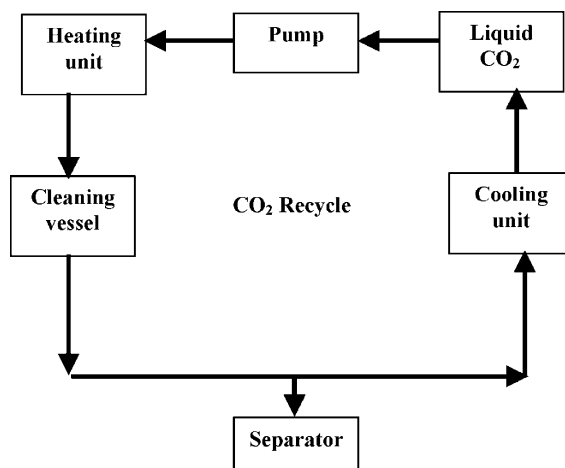


Figure 7. Basic components of a supercritical CO₂ cleaning system.

other organic contaminants can be removed from a surface even if it has a complex geometry or includes crevices. Figure 7 shows the basic components that comprise a supercritical CO₂ cleaning system. CO₂, which may be stored as a gas or in liquid form, is compressed above its critical pressure by a pump. The compressed CO₂ is then heated above its critical temperature in a heater, or sometimes in the cleaning chamber, making it supercritical. Any parts in the cleaning chamber are cleaned by exposure to the supercritical CO₂. Typically the cleaning chamber will include an impeller to promote mixing, see Phelps et al. (1994) and Williams et al. (1994). Supercritical CO₂-containing dissolved contaminants are then bled off to a separator vessel, where the supercritical CO₂ is decompressed and returned to the gaseous state. The contaminants remain in liquid form and are collected at the bottom of the separator, while the gaseous CO₂ is sent through a chiller to return it to a liquid form for storage to be reused again. This closed-loop recycling of the CO₂ means only a small portion of the cleaning solution has to be replaced over time due to system leakage. The cleaned parts can be removed from the chamber and are immediately ready for the next step in the manufacturing process, since no drying or rinsing is required to remove residual cleaning solution.

Tests on removal of oil from rings, washers, and plates showed elimination of 97 to 99.95% of the contaminants. Also, particulates were

successfully removed from computer disk drive's components with supercritical CO₂, see Novak et al. (1993). Supercritical CO₂ cleaning is a good candidate for water-sensitive or high-temperature sensitive parts when aqueous cleaning may not be feasible. Removal of moderately volatile substances, such as skin oil and mineral oil, was effective (by 99+%) and least effective (by 75% or less) on heavier contaminants such as silicone oil, see Williams et al. (1994). At this time, no large-scale production of supercritical CO₂ cleaning systems is underway (as is the case with aqueous cleaning systems and vapor degreasers), because the demand for the product is not high enough. This prevents supercritical CO₂ cleaning-system prices to take advantage of the economies of scale that take place with mass manufacturing.

High-pressure liquid CO₂ is also used for dry cleaning of garments. A company formed by DeSimone, Micell Technologies, offers integrated CO₂-based processes for dry cleaning, metal cleaning, and textile processing, called Micare, that uses liquid CO₂ as a solvent rather than perchloroethylene (perc), a potential groundwater contaminant and human carcinogen, see DeSimone and Tumas (2003). In fact, studies reported by researchers at the London School of Hygiene and Tropical Medical found that pregnant women who work in dry cleaners where perc is employed had a miscarriage rate of about 20%, nearly double of those not working in this industry, see Reuters (1997). Micell Technologies has launched a chain of more than 60 dry-cleaning stores throughout the United States, called Hangers Cleaners, which use a specially designed washing machine to clean clothes with beverage-grade CO₂ and specialty surfactants. The 60-lb-capacity machine uses a conventional rotating drum to agitate clothes and has a 40-minute cleaning cycle. It can recover the surfactants and about 98% of the CO₂ used, see Taylor et al. (2000).

Bottom-up technology, which is one of the principles of nanotechnology, attempts to synthesize nano-structured materials from nano-sized building blocks and promises new materials with superior properties than the existing ones (see more later and also Figures 8 and 9). Such a technology could help cut and possibly eliminate waste from manufacturing processes and fostering better materials. This is the essence of green chemistry which includes a more efficient production of the needed materials, elimination of hazardous waste material, and use of environmentally friendly supercritical solvents as alternatives to solvents that can damage the environment. With

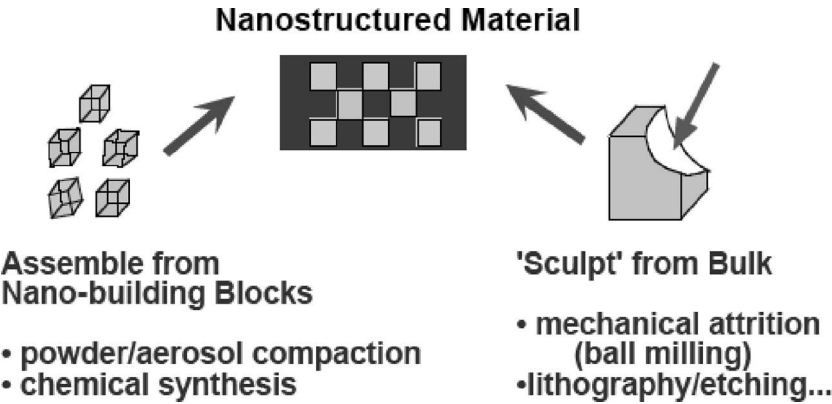


Figure 8. A diagram showing different nanostructure synthesis and assembly methods. Bottom-up (left) and top-down (right) approaches are exemplified. Hu (1999).

nanotechnology we can potentially reduce the amount of waste and with environmentally friendly supercritical fluids we can separate and destroy the waste safely. More interdisciplinary research is needed to bring these potentials into fruition and large-scale commercialization.

Lithography in Semiconductor Industry

The drive in silicon microelectronics is to build “smaller, faster, and cheaper” circuits and that has pushed the industry into nanoscale

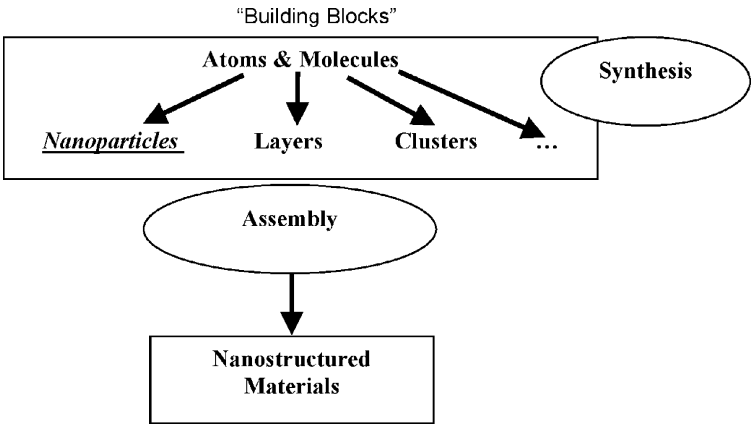


Figure 9. Nanostructured materials built from the “building blocks,” a “bottom-up” approach.

electronics, see Mathur (2002). The smaller the size of the transistor gate, the faster it can turn on and off, thereby raising the speed limits for the circuits using them. It should then be quite obvious why the semiconductor industry is shifting from manufacturing microchip to nanoscale feature-size chips. Semiconductor industry employs photolithography, a process by which a pattern on a photographic mask generates a pattern of light and dark on a wafer coated with a light-sensitive coating called photoresist. Next, chemical processing and baking harden the unexposed areas, which protects these unexposed regions (existed in dark) from the later stages of chemical processing. Although it was believed that feature sizes less than the wavelength of the light source were not possible due to blurring effects caused by diffraction, 70-nm features have been routinely made using a UV light source with a wavelength of 248 nm. It was made possible by optical proximity correction, phase shifting masks, and excimer lasers. In a sense, one can design an arrangement for the mask that, after diffraction takes place, delivers the desired pattern on the silicon chip, see Hutcheson (2004) and Takashi and Shinji (2000).

In the process of photolithography manufacturers primarily use wet-chemical processing involving hydroxylamines, mineral acids, elemental gases, and organic solvents during the different stages. In this process, a large amount of deionized water is used for rinsing. Chip manufacturers therefore consume thousands of gallons of chemicals and generate about 4 million gallons of waste water in a typical day. Copious amounts of isopropyl or other alcohols also are used as solvents. Considering that the feature sizes below 130 nm are needed for a new generation of integrated circuits, the surface tension of water no longer will allow the photoresist material to be easily removed from pores of low-dielectric materials or to penetrate smaller crevices for cleaning, see Figure 10. Supercritical CO₂ has very low surface tension and viscosity, allowing removal of photoresist masks, postetching, and other treatment residues from small structures. This is one key reason that supercritical fluid technology so naturally overlaps and is intertwined with nanotechnology. International Sematech, a research consortium formed by the semiconductor industry to help set standards, demonstrate new technology development, and solve common problems, has considered supercritical CO₂ as one enabling technology to solve the water problem.

SC Fluids, is a company that uses a process named SCORR (Supercritical CO₂ Resist Remover) for nanoscale semiconductor cleaning

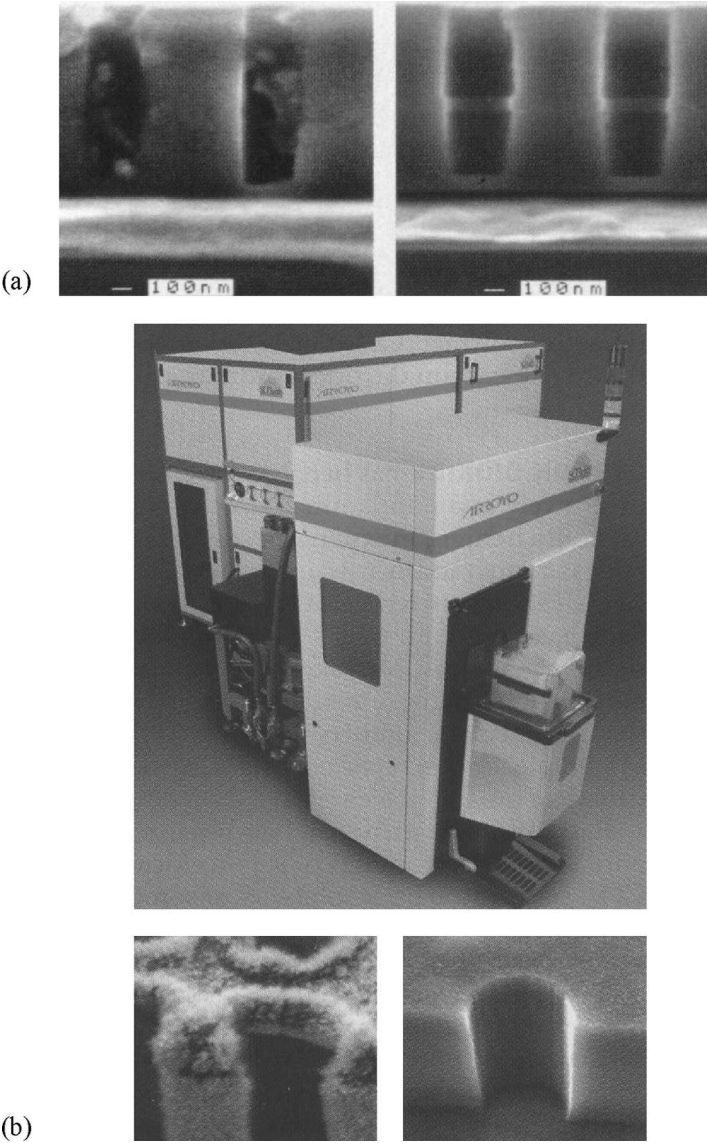


Figure 10. (a) Supercritical CO₂ technology developed by DeSimone's group in conjunction with Micell Technologies provides a water-free method to clean each residue during chip fabrication. (b) Cleaning machine by SC Fluids's Arroyo employs supercritical CO₂ to remove photoresists and etching residues during the patterning of semiconductor wafers. The bottom images are cross sections of a partially processed wafer (left) and a completely cleaned wafer (<http://www.scfluids.com/>).

purposes. This process was originally developed by LANL and was automated by SC Fluids with its Arroyo System, see Rothman et al. (2002). In addition, Dainippon Screen and Tokyo Electron Ltd. are other companies active in the advanced stages of developing supercritical CO₂ semiconductor processing methods. Professor DeSimone at North Carolina State University, is also working with the NSF's Science and Technology Center for Environmentally Responsible Solvents and Processes to build a demonstration facility for the "dry fab of the future" on campus. It is envisioned that all semiconductor processing could be done in a closed system using supercritical technology in 10 to 15 years, eliminating water and organic solvents and saving operating costs for clean room facilities.

Material Synthesis (Nanoparticles)

There are basically two major themes related to nanoscale science and technology. The first comes from the basis that any kind of material (metal, ceramic, polymer, semiconductor, glass, composite) is made from nanoscale "building blocks" that are themselves synthesized from atoms and molecules. Nanoparticles, including nanoclusters, -layers, -tubes, and self-assembled systems, are seen as "building blocks" of nanostructured materials and devices with tailored properties. Therefore, the controlled synthesis of "building blocks" and their subsequent assembly into nanostructures is one fundamental theme of nanotechnology. There are two approaches to build nanostructured materials: "top-down" and "bottom-up," see Figure 9. In the top-down method a macrosized material is reduced in size to reach the nanoscale dimensions. The photolithography used in the semiconductor industry is one example of this method. In the bottom-up strategy, we need these "building blocks" to assemble (or self-assemble) a nanostructured material, see Figure 10.

The second and most fundamentally important theme of nanoscaled science is that the nanoscale building blocks, because of their sizes below about 100 nm, impart to the nanostructures, created from them, new and improved properties and functionalities heretofore unavailable in conventional materials and devices. The reason is that materials in this size range can exhibit fundamentally new behavior when their sizes fall below the critical length scale associated with any given property. There is a recognition that this critical length scale defines the material structure

and organization, generally in the nanometer range, and that it ultimately determines the fundamental macroscopic properties of the material. Hence, essentially any desired property can be changed and engineered through the controlled size-selective synthesis and assembly of nanoscale “building blocks.”

Metals and ceramics produced by consolidating nanoparticles with controlled microstructures have been shown to possess properties substantially different from materials with coarse microstructures. New properties include greater hardness, higher yield strength, and ductility in ceramic materials. The band gap of nanometer-scale semiconductor structures increases as the size of the microstructure decreases, raising expectations for many possible optical and photonic applications. Nanoparticles have very high specific surface areas, and thus in their assembled forms there are large areas of interfaces. Researchers need to know in detail not only the structures of these interfaces, but also their local chemistries and the effects of segregation and interaction between the nanoscale “building blocks” and their surroundings. Therefore, knowledge on means of how to control nanostructure size and size distribution, composition, and assembly is an important aspect of nanoscience. Examples are now presented from selected areas to examine and appreciate a wide range of applications in which nanoparticles are employed.

Nanoparticles: Applications

Combustion and fuels: There are many proposed advantages of incorporating nanosized materials into fuels and propellants such as: (1) shortened ignition delay period; (2) much shorter burning time for nanoparticles than large particles, (assuming D^2 -law for particle burning, it implies a reduction of 100 in burn time when the diameter is reduced by a factor of 10); (3) shortened burn times result in a more complete combustion in small-sized propulsion systems; (4) higher specific surface area enhances heat transfer rates; (5) from the synthesis point of view, nanoparticles provide more flexibility in engineering new energetic fuel/propellants with desirable properties; and (6) nanoparticles can act as a gelling agent for liquids replacing inert or low energy material. For example, see Risha et al. (2002) for more details on nanometallic particles in the solid fuel matrix for hybrid rocket applications. More research is needed to fully understand and harness all the

potential gains of nanoscale materials in the context of the propulsion systems.

Simpson et al. (2000) and Gash et al. (2000), have pioneered the use of the sol-gel method (see the next section) as a new way of making nanostructured composite energetic materials. The synthesis of these nanocomposites takes advantage of the sol-gel process for production of aerogel, requiring supercritical fluid extraction as mentioned before. For this reason, a general understanding of the sol-gel process is also discussed here.

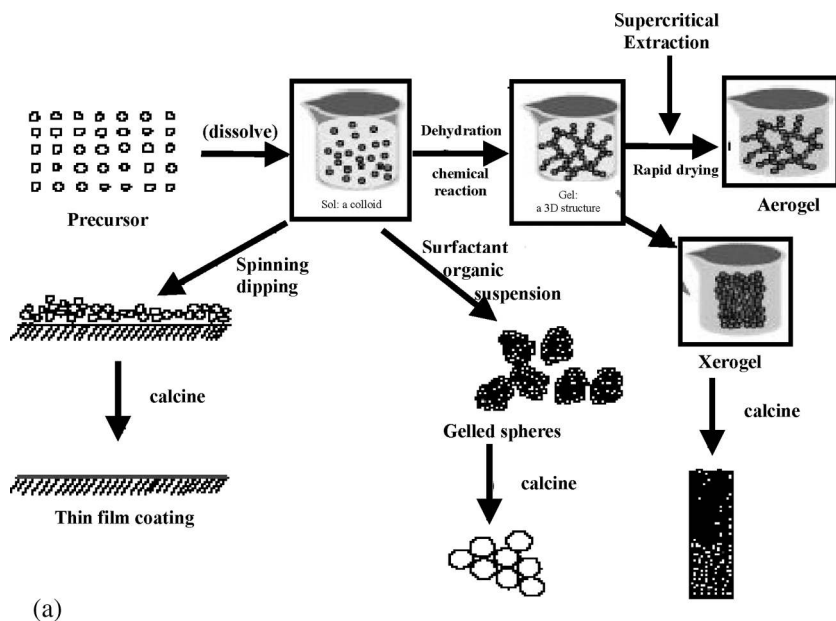
Sol-gel chemistry: The sol-gel chemistry involves the reaction of chemicals in a solution to produce a special kind of primary nanoparticles, called "sols." These can then be linked in a 3-dimensional solid network, called a "gel," with the open pores being occupied by the remaining solution. There are typically two different kinds of sol-gels: xerogel and aerogel. Aerogel process begins with a gel, called alcogel, made of silica (silicon oxide, or SiO_2 , which is glass or quartz) and a liquid solvent such as ethanol. Alcogels are made by polymerizing a silicon alkoxide, $\text{Si}(\text{OR})_4$, (where the R is an alkyl group) with water in a mixing solvent (such as ethanol). The reaction occurs by hydrolysis and water condensation, joining together the alkoxide molecules making silicon-oxygen bonds to form oligomers (minipolymers). The oligomers join together and form one giant molecule, which is the solid part of a gel. The silica matrix in the alcogel is filled with ethanol, having minute pockets 5 to 150 nanometers across. These tiny pockets of ethanol in the gel are called nanopores. A gel is really a colloidal system in which a network of interconnected solid particles spans the volume of a liquid medium. Typically, gels are free-standing solids but most of their volume is occupied by liquids. Aerogel is made by drying the alcogel and extracting the liquid from the solid silica component.

The alcogel's solid silica structure shrinks and collapses if the liquid solvent is dried by evaporation due to the capillary action. This implies that after the solvent has been completely taken out of the gel, the gel has collapsed and formed a dense solid that is only about 10% of the original volume of the gel. This solid is called xerogel (xero means "hard"). Products such as contact lenses and high-purity lenses are made in this way. Instead of evaporating the solvent, the gel can be supercritically dried. Supercritical drying is a process in which liquid can be removed from a gel without causing the gel to collapse. Supercritical

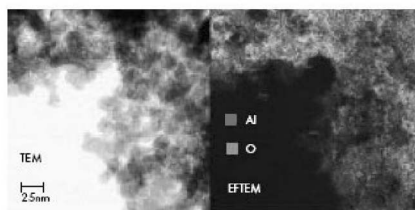
fluids have zero surface tension, contrary to ordinary liquids. Slow drying of alcogel under supercritical conditions is a better approach for removal of the liquid in the gel from the solid silica matrix without causing the silica matrix to collapse as a result of the surface tension. This is done by heating the gel past its solvent's critical temperature. Once the liquid is removed from the gel, the solvent can be vented off as a gas. The remaining solid is made of silica, with tiny pockets (nanopores) filled with air, and is 50–99% of the volume of the original alcogel. This solid is again an aerogel, see Leventis et al. (2002).

Since the pores of the aerogel structure have been largely kept intact through the use of the supercritical extraction method, the resulting solid is highly porous and light weight, with excellent uniformity given that the particles and the pores are both in the nanometer range. Figure 11 illustrates the sol–gel methodology and Figure 12 shows its very low thermal conductivity. The sol–gel approach is fundamentally different than most approaches to energetic material production in that it is a relatively simple methodology (e.g. chemistry in a beaker) performed at low temperatures. It can also be relatively inexpensive and has the promise of creating entirely new energetic materials with desirable properties.

One current promising nanocomposite being pursued by the researchers at LLNL involves the use of Fe_2O_3 which is generated using the sol–gel method. Nanocomposites are multicomponent materials in which, at least, one of the component phases has one or more dimensions (thickness, length, or width) in the nanometer range (often in between 1 to 100 nm). Fe_2O_3 is chosen because its “thermite” reaction with ultra fine grade (UFG) aluminum is highly exothermic (with only CuO and MoO_3 releasing greater heats of reaction). Thermitic reactions are extremely exothermic, based on reaction of an oxide with a metal to form a more stable oxide and the corresponding metal of the reactant oxide. Production of thermites by sol–gel method has two advantages: first, it reduces the fire hazards associated with conventional processing; second, it allows more intimate mixing of the fuel/oxidizer ($\text{Al}/\text{Fe}_2\text{O}_3$) components with precise stoichiometric control. An example of the high degree of mixing and uniformity between two nanophases is found in Figure 11(b), which indicates the excellent dispersion of Al and Fe on the nanoscale scale. The Fe_2O_3 was prepared by the use of an organic epoxide which was added to an Fe(III) salt solution resulting in the formation of nanoscale crystalline and amorphous Fe_2O_3 . The reaction to produce Fe_2O_3 was carried out in a solution which already contained



(a)



(b)

Figure 11. (a) Indicates the key steps that are required to synthesize aerogel (using a supercritical process) and xerogel (using a subcritical process). (b) Sol-gel $\text{Fe}_2\text{O}_3/\text{Al}$ nanocomposite. Simpson et al. (2000) and Gash et al. (2000) (See Color Plate 19 at the end of this issue).

the UFG aluminum. In this case, the nanoparticle of aluminum was sonicated (suspended in isopropanol and placed in an ultrasonic bath to break up any aluminum aggregates) before mixing with the Fe(III) salt solution. For this study, the UFG aluminum had an average aluminum particle size of approximately 35 nanometers. For details see Simpson et al. (2000) and Gash et al. (2000).

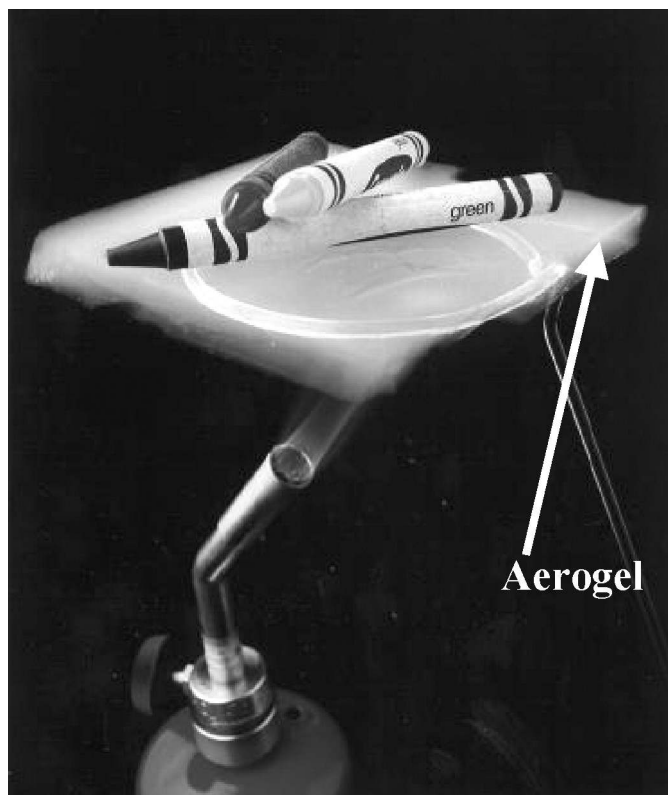


Figure 12. A sample of aerogel thermally shields the crayon from hot flame.

As sol-gel materials and their formation methodology advance, there are a number of possible application areas that are envisioned. These include: (1) high-temperature stable, nondetonable gas generators, (2) adaptable flares, (3) combustion primers, and (4) high-power, high-energy composite explosives. In addition, the sol-gel chemistry may have advantages of being more environmentally acceptable, compared to some other methods of producing energetic materials.

Monopropellants: Consider another example in which the marriage of supercritical fluids and nanoparticles occurs in the context of monopropellants. The use of a catalysis in the field of propulsion began just before World War II in Germany with the catalytic decomposition of H_2O_2 through injection of liquid permanganate salts. After the war,

different projects used kerosene with H_2O_2 and a silver-screen catalyst (bipropellant propulsion). The beginning of the space program led to the replacement of H_2O_2 by the more stable hydrazine N_2H_4 as the monopropellant, using $\text{Ir}/\text{Al}_2\text{O}_3$ as the catalyst. However, the toxicity of hydrazine led to the research for a possible nontoxic or “green monopropellants” substitutes. The candidate substitutes are energetic aqueous ionic mixtures containing an oxidizer (for example, HAN or hydroxylammonium nitrate $[\text{NH}_3\text{OH}] + [\text{NO}_3]^-$) and a fuel (such as glycine, methanol).

The problem is that, unlike hydrazine, the decomposition of such a mixture releases very hot gases with temperatures reaching over 1400°C . Hence, the current challenge is to find a catalyst/substrate system that, (1) triggers the decomposition of the monopropellant mixture at low temperatures, (2) limits the formation of nitrogen oxides during the thermal decomposition, (3) keeps good thermal stability and specific surface area at high temperatures, and (4) avoids the loss of active phase under the propellant flow, see Courtheoux et al. (2003). In their work, a catalyst support (silica doped alumina) was prepared via the sol-gel approach using two drying methods leading to xerogel and aerogel. The sol-gel alumina samples doped with silicon sustains thermal treatment at 1200°C , or more, for several hours. The active phase (palladium as catalyst) was introduced on the support surface through two methods. First, a precursor was added before the sol formation in “one step” and, second, by “impregnation” of thermally stabilized support from an aqueous metal precursor solution, see Figure 13. It was shown that the catalyst prepared by the impregnation procedure led to metallic nanoparticles (4 to 10 nm) smaller than those prepared by a one-step method (larger than 50 nm), due to sintering effects at high temperature. Finally, the one-step procedure led to an increase of the thermal stability for the aerogel samples, but the catalytic activity at low temperature was less efficient in comparison with xerogel samples. The impregnation catalysts always displayed a better activity in relation to the lower size of the metallic nanoparticles, see Figure 13.

Catalysis: Surface chemistry has greatly advanced our understanding of catalytic reactions, a subject of significant importance from scientific, technological, and social perspectives. Three examples of catalytic reactions of importance are the synthesis of ammonia from nitrogen and hydrogen, a process that made possible the large scale production of

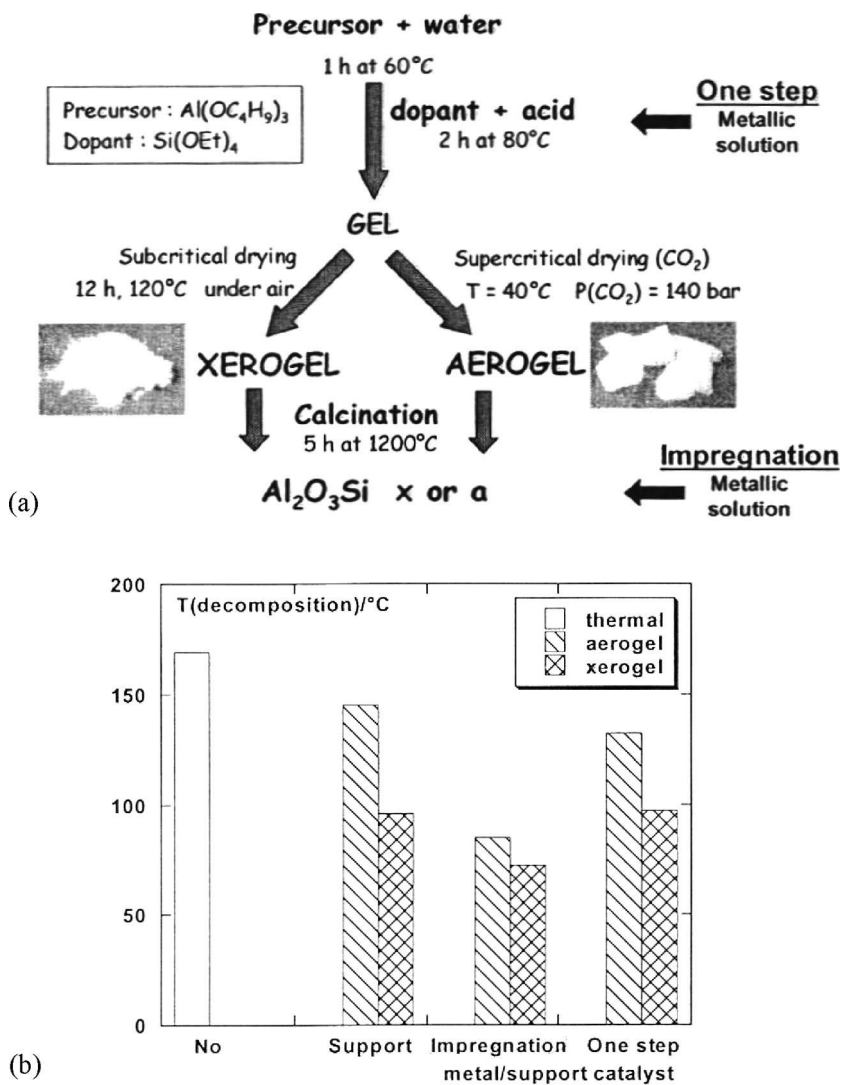


Figure 13. (a) Schematic diagram for the preparation of the supports and the catalysis. (b) Decomposition temperature of 70 wt.% HAN-water mixture with different catalyst supports. Courtheoux et al. (2003).

fertilizers and explosives, breakdown of nitric oxides in the exhaust of automotive engines and as a result alleviating the problem of acid rain and mitigating the effects of other harmful pollutants in the atmosphere,

and finally, removal of sulfur from fuels, a process that also has implications for atmospheric pollution reduction.

A large majority of catalysts used in industry are high-surface area solids onto which an active chemical species (catalyst) is dispersed in the form of very small particles. The active components (nanoparticles) have dimensions of about 1 to 20 nm. A good example of this is the catalyst bed for the catalytic converter used in the exhaust system of automobiles, see Figure 14 from Bell (2003). It consists of a honeycomb whose walls are covered with a thin layer of porous aluminum oxide (alumina) as a wash coat and is impregnated with nanoparticles of Pt, Rh, Ce, zirconia, and lanthanum.

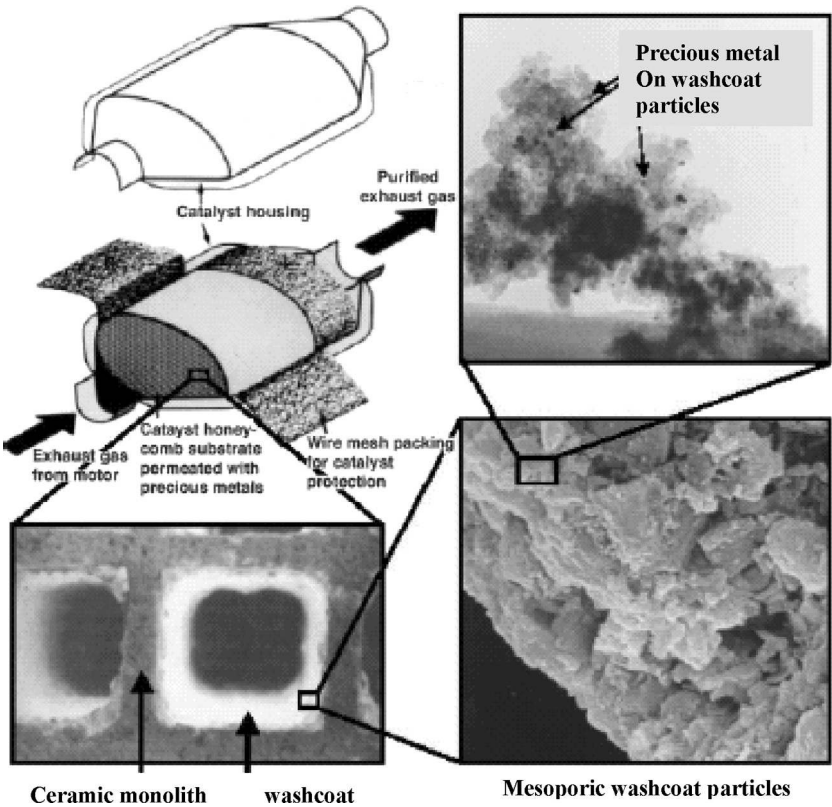


Figure 14. Shows the placement of nanoparticles in automotive catalytic converters. Bell (2003).

The basic premise here is that the local size and composition of the catalyst particles affect their activity and selectivity. As stated before, particles in the approximate range of 1 to 50 nm show chemical and physical properties that are intermediate between those of the elemental and bulk material. Catalyst performance can be sensitive to particle size mainly because the surface structure and electronic properties can change greatly in this size range. As an example, Titania-supported Au nanoparticles have been shown to be active at ambient conditions for oxidation of CO to CO₂ and can be employed for the reduction of CO in buildings by incorporating them into the interior walls. Figure 15 shows the activity of the Au nanoparticles as a function of their size. Their activity is very sensitive to the size and peaks at nearly 3 nm. This observation was explained to be as a result of the oxidation of the Au atoms that are in contact with the support, and it beautifully illustrates the importance of tuning the electronic properties of the metal nanoparticles to achieve high catalytic activity, see Bell (2003).

Carbon nanotubes offer interesting possibilities as supports for metal particles. Recently, it was shown that Ir nanoparticles deposited into tube bundles are more effective for the decomposition of hydrazine than Ir on a conventional support such as alumina. This is of potential interest for hydrazine-fueled thrusters used for space vehicles, see De Jong and Ceus (2000).

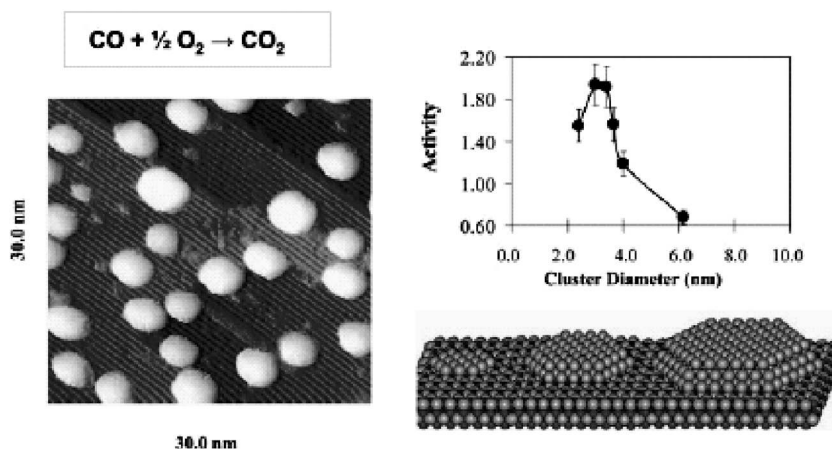


Figure 15. Effects of nanoparticle size on the activity of titania-supported Au for the oxidation of CO. Bell (2003).

Materials: Although applications of the nanoparticles in material science to enhance mechanical properties of the materials are numerous, only one recent interesting application which has been commercialized on a large scale is presented here. This method uses calcium carbonate (CaCO_3) nanoparticles as a cost-effective means of increasing the toughness (impact strength) of polyvinylchloride (PVC) and polypropylene (PP) copolymer without compromising its rigidity. Toughness refers to a material's ability to absorb mechanical energy without fracturing. A tough material can absorb mechanical energy with either elastic or plastic deformation. In general, high-impact unfilled resins have excellent toughness. However, low- to moderate-impact resins can also display considerable toughness if the material has sufficiently high ultimate strength. Toughness is often measured by the area under the stress-strain curve of the material. Brittleness is the lack of toughness. Plastic materials that are brittle frequently have lower impact and higher stiffness properties. Many glass-reinforced and mineral-filled materials display brittleness.

The 15 to 40 nm sized CaCO_3 particles are produced by a reaction of calcium hydroxide and carbon dioxide in a rotating reactor. Proprietary surface modification techniques are then applied to the nanoparticles to enable compounding of masterbatches. The masterbatches can be manufactured using standard twin-screw compounding equipment. Nano- CaCO_3 masterbatches, in which particle loadings are typically 70 to 80%, can then be utilized to enhance the impact properties of the products such as PVC window profiles, where they can partially replace impact modifiers such as chlorinated polyethylene (CPE) and poly-methacrylate-butadiene-styrene (MBS). Interestingly, flexural modulus is usually enhanced as well, see Figure 16. The key in using Nano- CaCO_3 to enhance the toughness of plastics lies in the dispersion of the nanoparticles in the polymer matrix. Nanoparticles have a very high surface activity, resulting in a tendency for them to agglomerate. Special surface modification of the nano- CaCO_3 particles was carried out to enable preparation of the masterbatches using conventional techniques. This enables effective dispersion of these nanoparticles in the matrix. For more information see Bartczak et al. (1999).

It is generally thought that the mechanism of plastics toughening with nanoparticles is the large surface area of the nanoparticles, which causes a large amount of crazing (microfracturing) within the polymer matrix. These microfractures act to dissipate impact energy. At the same time the matrix in the internanoparticle space is thought to undergo

Sample	Composition (pph)			Single-Notch Impact Strength (kJ/m ²)	Flexural Modulus (MPa)	Tensile Strength (MPa)
	PVC	Nano-CaCO ₃	CPE			
1	100	0	8	14.9	2180	38.8
2	100	8	8	81.4	2210	38.6

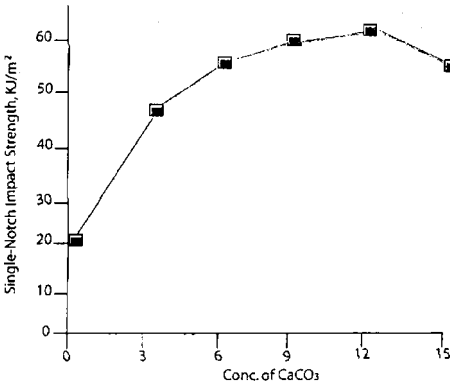


Figure 16. Properties of nano-CaCO₃/PVC/CPE compounds (top). Single-notch impact strength of nano-CaCO₃/PP composites against concentration of CaCO₃ (bottom). Bartczak et al. (1999).

plastic deformation on impact, which also results in dissipation of external impact forces, hence achieving toughness. However, the plastic-toughening effect of inorganic nanoparticles does require the polymer matrix to have an inherent toughness. In a brittle plastic (PVC), a small amount of impact modifier (e.g., CPE) is needed in the formulation. The nano-CaCO₃, and the CPE then exhibit a synergistic toughening effect within the nano-CaCO₃/PVC/CPE composite system (in commercial application: 4pph of CPE and 4pph of nano-CaCO₃ is considered optimum), see Figure 17.

Biomedical engineering: Total-hip replacement is a common surgical operation these days. Usually, the socket of the implant is made of ultra-high molecular weight polyethylene (UHMWPE). However, the surfaces of this polymer can be damaged or degraded as the ball of the artificial joint moves around in the socket. This will cause production of small particles of UHMWPE that can result in problems and implant failure. Researchers, in particular Poliakoff’s group at Nottingham University, developed a supercritical fluid method for impregnating tiny metal

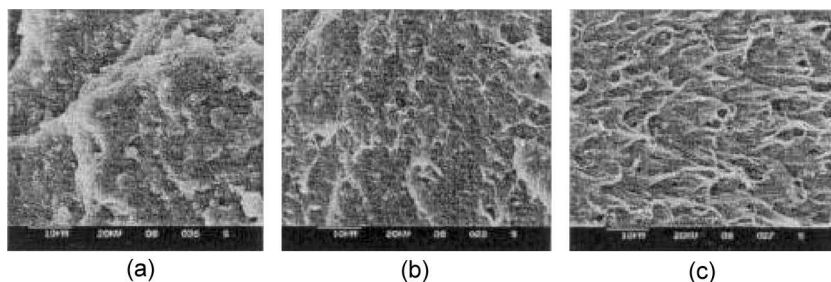


Figure 17. Shows the fracture surface of nano-CaCO₃/PVC composites. (a) PVC/CPE/CaCO₃ (100:8:0 ratio); (b) PVC/CPE/CaCO₃ (100:8:4); (c) PVC/CPE/CaCO₃ (100:8:8). When no nano-CaCO₃ is used in (a), the fracture surface of the composite is uneven, the typical appearance of a brittle fracture. When 4 pph is added in (b), fibrils begin to appear on the fracture surface of the PVC composite. At 8 pph in (c), obvious fibril form on the fracture surface on impact, indicating large amount of craze generated in the PVC matrix. Bartczak et al. (1999).

particles in the polymer matrix to improve the properties of the UHMWPE. They have developed silver precursors for the preparation of silver/UHMWPE composites by impregnation using supercritical CO₂. Figure 18 shows a sample of the hip joint and TEM of the polymer matrix containing nanoparticles, see Mandel et al. (1998), Cooper et al. (1993), and Howdle et al. (1994).

Medical: Tumors can only grow if they find the nourishment they need through new blood vessels. Cancer researchers have spent years working to starve tumors by blocking this blood vessel growth, or “angiogenesis,” with mixed success, see Hood et al. (2002). A team from Scripps Research Institute has approached the problem of choking off tumor vessels from a novel angle: The researchers packed a tiny nanoparticle with a gene that forces blood vessel cells to self-destruct, then they “mailed” the nanoparticle to blood vessels feeding tumors in mice.

The study, led by vascular biologist David Cheresh of the Scripps Research Institute, draws on research in a number of fields. In the mid-1990s, Cheresh and others found signatures specific to different types of blood vessels that they used as target “zip codes.” One of these, belonging to a class of membrane proteins called integrins, is apparently always present on angiogenic, or newly growing, blood vessels but rarely on established ones. The integrin, $\alpha_v\beta_3$, has another quality that would turn out to be convenient: It can propel viruses or other small particles into cells.

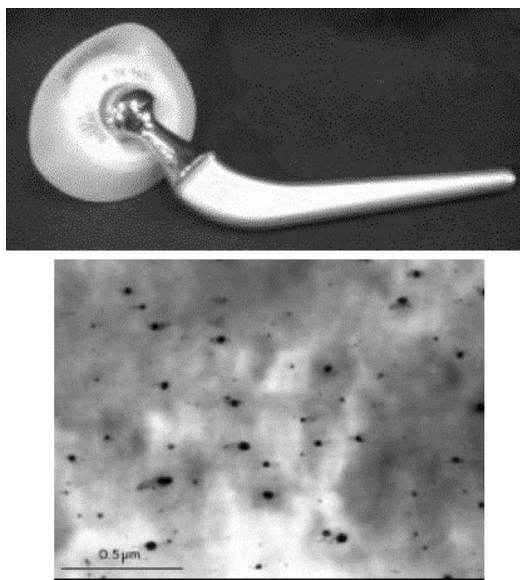


Figure 18. A sample of the hip joint and TEM of the polymer matrix containing nanoparticles. (Mandel et al., 1998).

Cheresh's team, assisted by organic chemist and radiologist Mark Bednarski of Stanford University, designed a lipid based nanoparticle that would target new blood Vessels. The nanoparticle's surface is studied with molecules that bind to $\alpha v \beta 3$, and embedded with copies of a mutant form of the *Raf 1* gene that disrupts *Raf*'s normal activity, see Figure 19. "It is a very provocative paper, which I think will become a landmark in angiogenesis research," says antiangiogenesis pioneer Judah Foikman of Children's Hospital in Boston. Adds Philippe Leboulch, a gene therapist at Harvard Medical School in Boston: "They achieved tumor regression—and they started with tumors that were quite large for mice." Despite their enthusiasm, however, researchers are walking around the landmines in cancer treatment, where hopes have been raised and dashed many times.

Nanoparticles: Synthesis Using SCF

As indicated above, although nanoparticles made of different materials have different enhanced physical, chemical, or optical properties, they

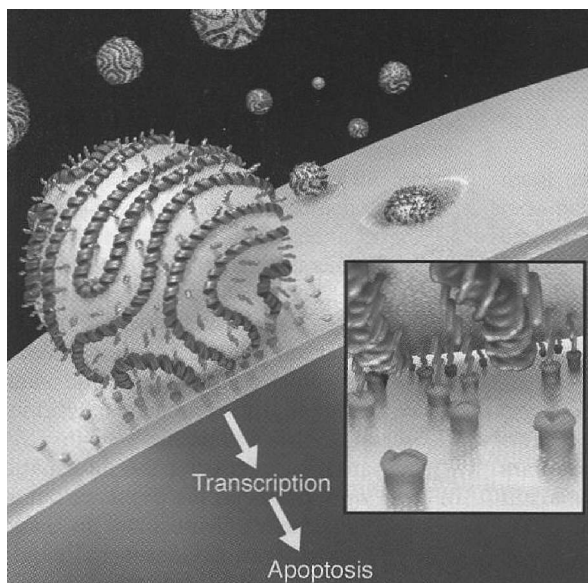


Figure 19. Nanoparticles packed with targeting molecules (red) anchor to integrins (blue) on the outside of a tumor blood cell before shuttling mutant DNA (green) inside. Hood et al. (2002).

are considered as important building blocks in nanotechnology. For this reason alone, research on methods for synthesis of nanoparticles of different materials is considered an important pillar of this new technology. In what follows, only those methods that employ special properties of SCFs are discussed.

Rapid expansion supercritical solution (RESS): In early studies, Krukoni (1984) demonstrated an application of the RESS method for particle synthesis. Small particles and fibers of many materials including aluminum isopropoxide, dodecanolactam, polypropylene, β -estradiol, ferrocene, navy blue dye, and soybean lecithin were produced by this method. In the RESS process a solute is dissolved in a supercritical fluid and then the solution is rapidly expanded through a small nozzle or an orifice into a space of lower pressure, see Eckert et al. (1996). The rapid reduction of density (as a result of lowered pressure) to the subcritical range causes rapid precipitation of the solute and subsequent formation of nanoparticles. The supercritical

fluid is obtained by heating and pressurization of the solution from room temperature, allowing the expansion phase of the process to occur at a known concentration (as opposed to continuously extracting the solute using an extraction column), see McHugh and Krukons (1994a). Because solubilities in SCFs can be higher than those under ideal gas condition by many orders of magnitude (about a million times), rapid expansion from a supercritical pressure results in extremely high supersaturation and consequently homogeneous nucleation of the solute, forming a narrow size-distribution of particles. A variety of product morphologies, such as particles, films, and fibers from organic, inorganic, and polymeric materials are possible, see Peterson et al. (1987) and Smith et al. (1986).

As an example, supercritical water is used as a solvent with chips of high purity SiO_2 glass in an autoclave as shown in Figure 20, see Peterson et al (1987) and Smith et al. (1986). The autoclave at a subcritical temperature and pressure of 590 bar was equilibrated for hours. Then the valve was opened and a heated tube zone raised the temperature to a supercritical value. Rapid expansion in an expansion nozzle (5 mm length, 60 μm i.d. s.s. tube) into an evacuated chamber (0.1 to 1 bar), to minimize potential health hazards, produced fine powders of silica. A dramatic change in the dissolving power experienced by a solute as it rapidly expands from a supercritical state (significant dissolving power) to a subcritical state (negligible dissolving power) started rapid nucleation and growth processes of the low vapor pressure solute leading to the formation of fine particles. The expansion process is divided into three stages: subcritical expansion (through the length of the nozzles itself), a brief supersonic free jet expansion (immediately upon exiting the nozzle), and the final stage in which the jet interacts significantly with the background gas in the expansion region. Flow through the nozzle is choked and expands adiabatically reaching the speed of sound at the exit. A set of shock fronts separates the isentropic region from the other downstream parts. Within the supersonic region, the expansion process is complex and a jet may enter the two-phase expansion region. Assuming adiabatic expansion at an exit pressure of 600 bar, the final state (single- or two-phase) of the expanded gas (with low concentration of solute) depends on the exit temperature, see Figure 21. Operation of the RESS process in the single-phase solvent expansion mode offers the advantage of collecting solute products in the "dry" state, with no liquid solvent incorporated in the product structure. A better understanding of

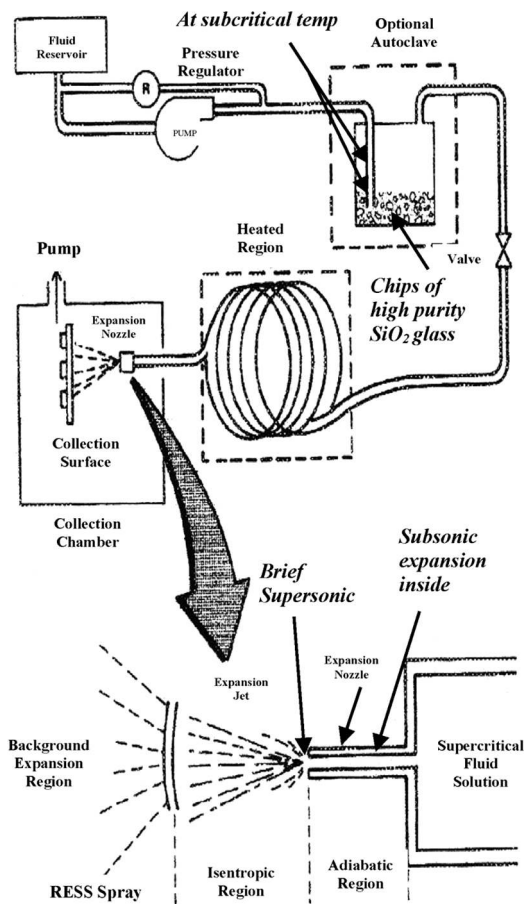
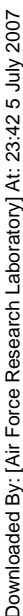


Figure 20. Schematic illustration of the RESS setup as used for supercritical water. The RESS expansion is also shown through the nozzle. Peterson et al. (1987).

the RESS expansion processes which affects nucleation and growth processes is needed for a better control of the physical properties of the end products.

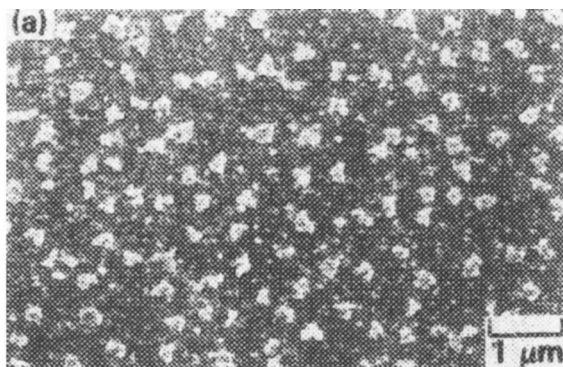
Supercritical antisolvent method (SAS): This method of micro- and nano-particle synthesis uses the precipitation processes in supercritical solutions known as Supercritical AntiSolvent (SAS), see Debenedetti et al. (1993) and Darr and Poliakoff (1999). The case of interest here is when a solution is added or injected into a supercritical fluid acting



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***Low
concentration
of silica:
significantly
smaller in size***



***High
concentration
silica: X-ray
amorphous
silica
particles ~ >
0.2 micron***

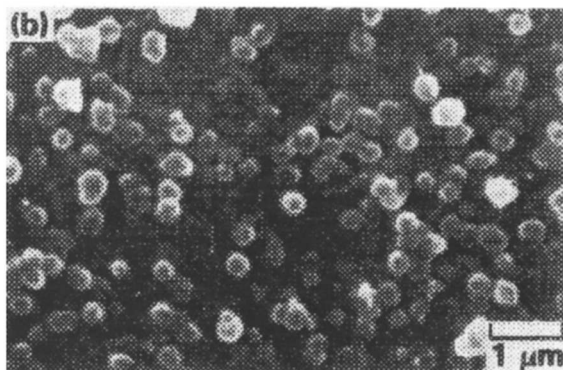


Figure 22. Silica products prepared using RESS process SiO_2 powders synthesized using different concentrations of silica in the SCF-water solution. Peterson et al. (1987).

This method has been employed in the production of a variety of fine particles and powders from pharmaceuticals, pigments, polymers, proteins, and explosive materials. For example, for polymers, Mawson et al. (1997) utilized a toluene solution of polystyrene sprayed into compressed CO_2 . The particle size was adjustable within a wide range (100 nm to 20 μm) by varying the CO_2 density and temperature. Higher CO_2 densities and lower temperatures resulted in smaller particles. Application to explosives has been demonstrated by Gallagher et al. (1992). Very small crystalline particles (<200 μm) of cyclotrimethylene-trinitramine (RDX) were made using subcritical and supercritical CO_2 as the antisolvent with a variety of solvents.

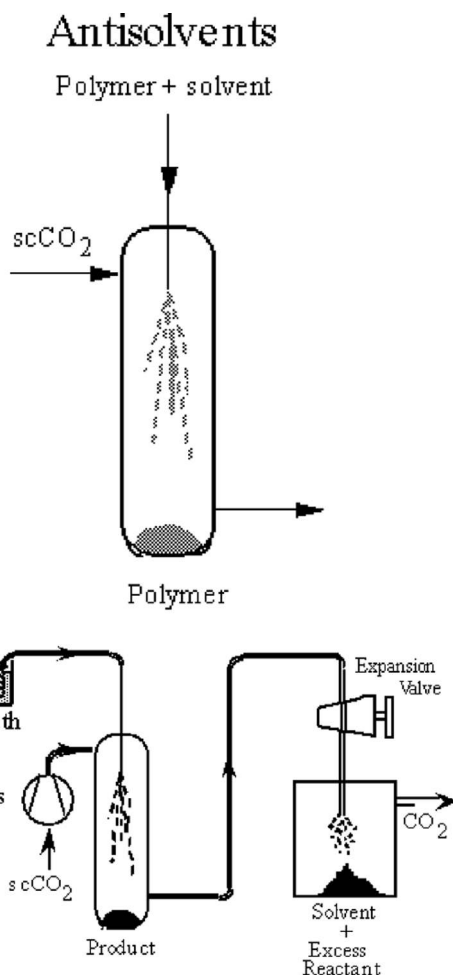


Figure 23. Micro and nano- particle synthesis via antisolvent method. “scCO₂” means supercritical CO₂.

Nanoparticles in SCF and reverse micelle: A micellar system, being generally stable and macroscopically homogeneous, usually consists of three components to facilitate separation: two liquid phases that are immiscible and an amphiphilic surfactant. Normal micelles (or simply micelles) consist of spherical oil droplets in a bulk water phase and reverse micelles consist of water droplets in a bulk oil (organic solvent)

phase. A surfactant molecule is formed by two parts with different affinities for the solvents. One of them has affinity for water (polar solvents) and the other for oil (non-polar solvents). Hence, in a normal micelle, the polar end of the amphiphilic surfactant molecules are extending out of the micelle, while in a reverse micelle, the nonpolar end is out of it. The size of these so-called droplets can be varied by changing the oil/surfactant and water/surfactant ratios for normal and reverse micelles, respectively. The nanoscale regions in the micellar structures act as templates for manufacturing semiconductor and metal nanoparticles. In these systems, the contents of different micellar spaces (i.e., within the micelles) undergo exchange when the micelles collide, creating opportunities for mixing and reactions between the reactants brought by different micelles.

Recently, there has been much interest in using the properties of microemulsion phases in SCFs, particularly a reverse micelle or microemulsion based on CO_2 . Water and CO_2 are the two most abundant, inexpensive, and environmentally compatible solvents. Reverse micelles formed in supercritical CO_2 allow highly polar or polarizable compounds to be dispersed in this nonpolar fluid. However, most ionic surfactants with long hydrocarbon tails, such as sodium bis(2-ethylhexyl)sulfosuccinate (AOT), are insoluble in supercritical CO_2 . The use of ionic surfactants with fluorinated tails provide a layer of a weakly attractive compound covering the highly attractive water droplet cores, thus preventing their short-range interactions that would destabilize the system. Experiments indicated that these CO_2 -philic ionic surfactants do not form very stable water-in- CO_2 microemulsions, especially when the water cores contain high concentrations of electrolytes. This problem was recently remedied by use of a conventional AOT and a fluorinated cosurfactant, see Jackson and Fulton (1998) as shown in Figure 24. In this manner, a very stable water-in- CO_2 microemulsion containing a relatively high concentration of silver nitrate can be formed, see Johnston et al. (1996).

For example, using a mixture of AOT and a perfluoropolyether (PFPE) co-surfactant, the investigators changed the ratio of water-to-AOL until an stable microemulsion system was achieved. This method was employed to synthesize and stabilize metallic silver nanoparticles (5 to 15 nm) in supercritical- CO_2 using an optically transparent, water-in- CO_2 microemulsion.

In one case, a mixture of AOT (12.8 mM) and the perfluoropolyether-phosphate ether (PFPE-PO₄, 25.3 mM) at a water-to-surfactant

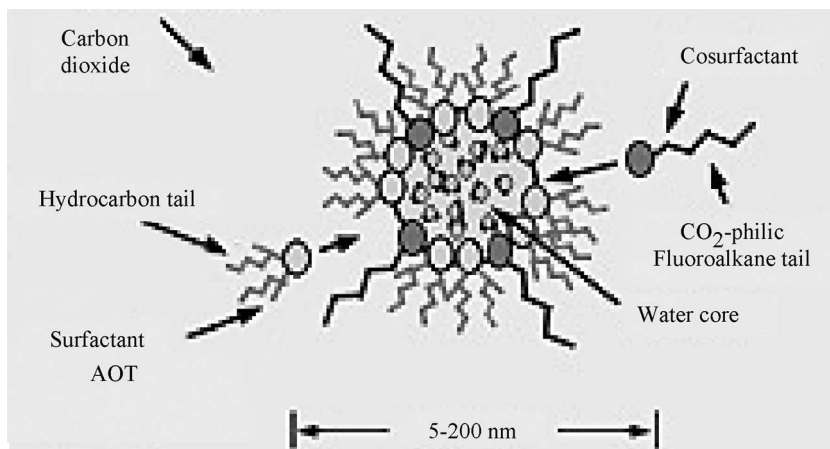


Figure 24. Structure of CO₂ microemulsion droplet (a reverse micelle) formed with the aid of AOT surfactant and CO₂-philic fluoroalkane tail cosurfactant. Jackson and Fulton (1998).

ratio of 12 was prepared. The microemulsion containing AgNO₃ (0.33 mM) was optically transparent and stable in supercritical CO₂ for hours. To make metallic silver nanoparticles, a reducing agent was required. Here, NaBH(OAc)₃, was injected into the supercritical fluid microemulsion system to reduce Ag⁺ in the water core to Ag, see Ji et al. (1999) for more details. Within minutes, the formation of Ag nanoparticle in the microemulsion system was observed after the introduction of the reducing agent. The formation and stability of the Ag nanoparticles was monitored in situ by UV-Vis spectroscopy utilizing the 400-nm band originating from the surface plasmon resonance (see Appendix) of Ag nanoparticle crystals, see Figure 25. The supercritical fluid solution stayed optically clear with a yellow color due to the absorption of the Ag nanoparticles. Bandwidth analysis of the plasmon emission showed particle sizes of about 4 nm, see Figure 25.

However, TEM images suggested particle sizes of approximately 5–15 nm. Note that in this case, the Ag nanoparticles were collected via the RESS (rapid expansion of supercritical fluid solution) technique using a 50 μm i.d. PEEK restrictor, see Smith et al. (1987). Other metallic nanoparticles including Pd and Cu have been manufactured using this approach.

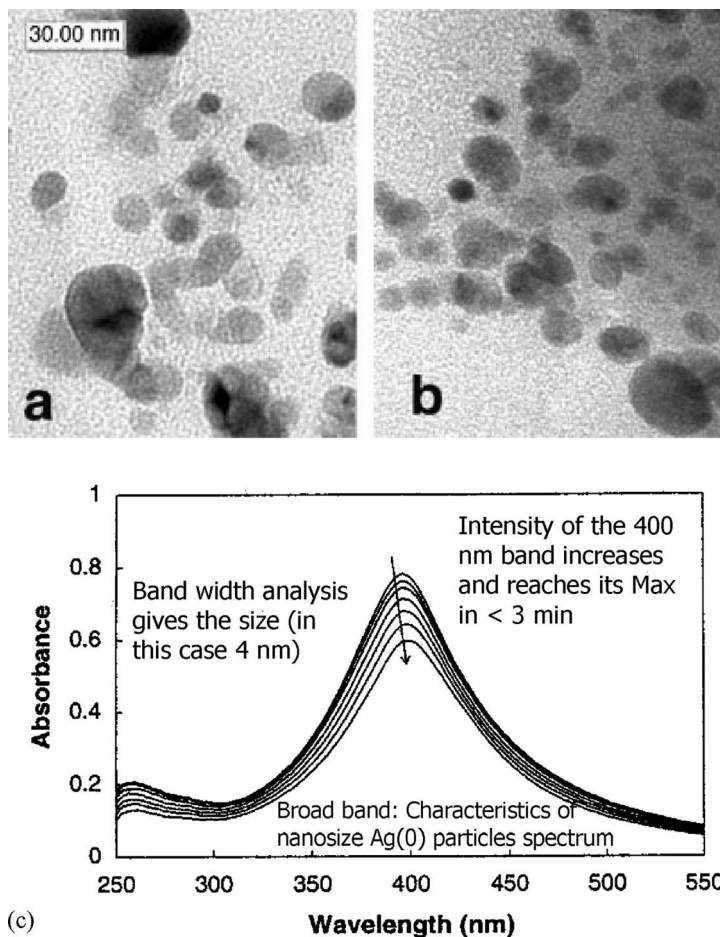


Figure 25. (a) TEM of silver particles synthesized in liquid CO_2 (25°C and 300 bar), and (b) supercritical CO_2 (35°C and 367 bar), (c) Series of UV-vis spectra of Ag(0) nanoparticles dispersed in microemulsion formed in supercritical CO_2 (35°C and 367 bar) collected at intervals of 10 min. Spectra were acquired at evenly spaced intervals over the course of an hour after their formation. Ji et al. (1999).

In an extension of this method, collision and exchange of the contents between two water-in- CO_2 microemulsions is utilized to synthesize nanomaterials. Using microemulsions carrying different ionic species in the water cores, silver halide nanoparticles were produced in supercritical CO_2 . Figure 26 shows the dynamics of the two microemulsions explaining formation of the AgI nanoparticles.

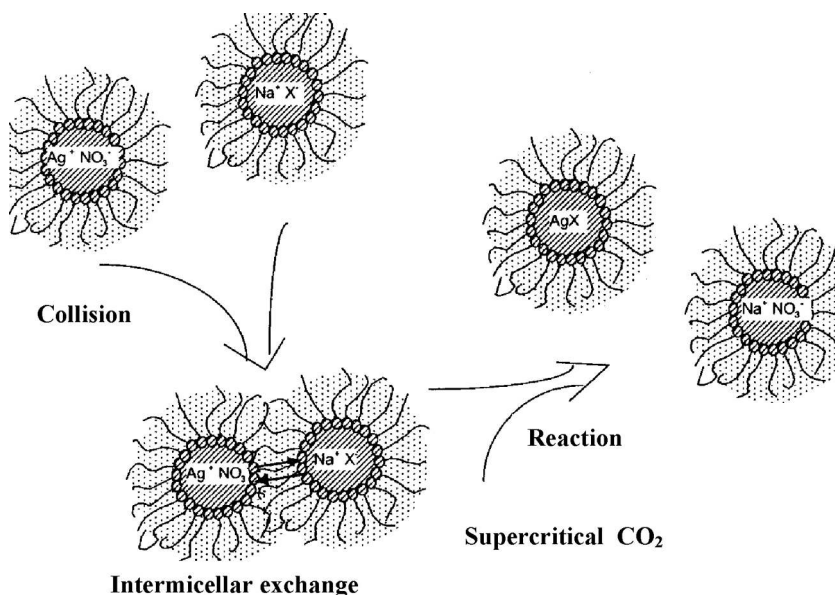


Figure 26. The proposed mechanism for the formation of AgI nanoparticles in supercritical CO₂ by mixing two water-in-CO₂ microemulsions with one containing AgNO₃ and the other NaI in the water core. Sun (2002).

Finally, Sun et al. (2001) varied the basic RESS method by expanding the supercritical solution into a liquid rather than a gas in an effort to eliminate agglomeration processes responsible for growth of particles above the nano-size range. They called it RESOLV, standing for rapid expansion of supercritical solution into a liquid rather than a gas. In essence, one reactant is dissolved in the SCF solution and another in the liquid receiving the SCF solution after expansion. For example, Cd²⁺ ions in a sprayed SCF ammonia solution react with S²⁻ in a receiving liquid ethanol solution to form CdS nanoparticles (quantum dots). This RESOLV method is then coupled with a water-in-CO₂ microemulsion system and was designed to synthesize a variety of nanoparticles. In one demonstration, a reverse micellar solution of aqueous-AgNO₃/PFPE-NH₄ in CO₂ was rapidly expanded by way of a 50 μm capillary nozzle into a room-temperature solution of NaBH₄ in ethanol for chemical reduction. The silver nanoparticles produced in the rapid expansion/chemical reduction were protected from agglomeration in the presence of PVP polymer and discovered a stable solution. TEM analysis of the

nanoparticles showed an average size of 7.8 nm with a size distribution standard deviation of 2.5 nm. The importance of this method is that the formation of nanoparticles occur under ambient condition outside the supercritical chamber, preventing difficulties associated with the in situ reaction method regarding the collection of the as-prepared nanoparticles, see Sun (2002).

Also, silver nanoparticles were manufactured by Sun et al. (1999) by first preparing a homogenous solution of ammonia and AgNO_3 in a syringe pump and then heated to the desired temperature. The nanoparticles of Ag were formed through rapid expansion of the supercritical solution of AgNO_3 in ammonia (4000 psia and 160°C) into room-temperature ethanol and hydrazine (N_2H_4 , as reducing agent) solution. A stable suspension of nano-sized Ag in ethanol was formed under the protection of a stabilizing agent. An intense UV-vis absorption band at about 410 nm was characteristic of the plasmon absorption from the nanoparticles. TEM images suggested an average size of 5.6 nm with size distribution of 0.78 nm, see Figure 27. Nanoparticles of other metals such as copper, nickel, cobalt, and iron were reported using this method.

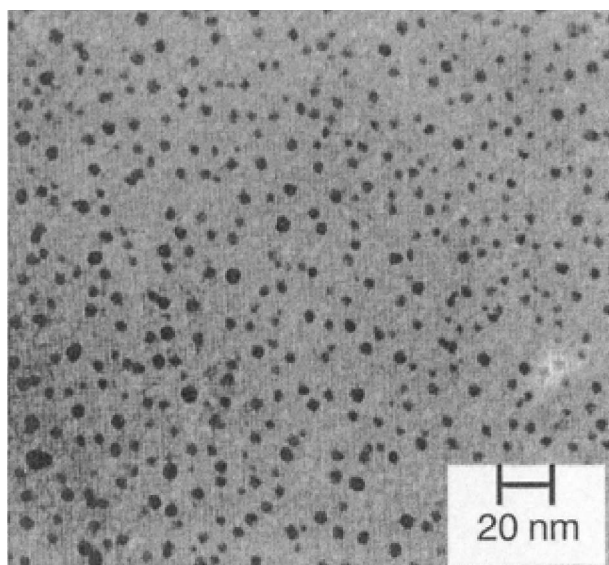


Figure 27. TEM images of the Ag nanoparticles prepared via RESOLV with N_2H_4 reduction, Sun et al. (1999).

Supercritical Fluids and Polymers

The word polymer comes from Greek, *polymers*, or having many parts and it describes a long chain of molecule with a repeating pattern, or macromolecule. Figure 28 shows the historic importance of polymeric materials as compared to metals, composites, and ceramics. World consumption of plastics both by weight and volume has surpassed steel as the material of choice in many applications. Historically, it was Professor Herman Staudinger, an outstanding German academician, who first proposed the possibility of high-molecular weight (i.e., long chain) molecule explaining the polymers. He postulated that rubber is composed of long molecules (polymers) in which the recurring unit (monomers) are combined by primary valences or covalently bonded (a bond having a shared pair of electrons).

A brief discussion of the viscoelastic properties of polymers is helpful in understanding the effects of supercritical fluids on polymers. Figure 29 is a plot showing the modulus of elasticity ($E = \sigma/\epsilon$, where σ is stress and ϵ is strain) as a function of temperature, indicating five regions of viscoelasticity in amorphous polymers (solid line), plus the

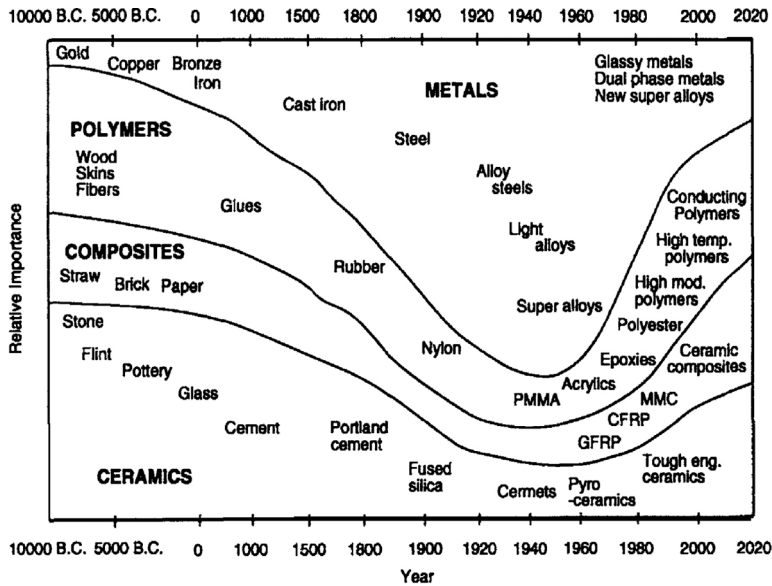


Figure 28. Relative importance of material development throughout the history. Ashby (1987).

crosslinked (dotted line) and semi-crystalline behaviors (dashed line). In area 1, the polymer is stiff and is called the glassy region. In area 2, the polymer softens and is referred to as the glass transition region. The temperature at which such a softening occurs is called the glass transition temperature, see Figure 29. In the plateau region, area 3, the polymer behaves rubbery. Finally, in the liquid flow region, area 5, the polymer can flow. If the polymer is crosslinked sufficiently, it does not soften, but follows the dotted line. However, if the polymer is semicrystalline, it may follow the dashed line. At the melting temperature, the modulus falls off rapidly, usually into rubbery flow or liquid flow regions.

CO₂ is a good SCF and it is used in many polymer processes. Since CO₂ is a gas at room conditions, its convenient removal from polymeric products is possible without costly drying and solvent removal processes. DuPont has recently announced plans for a major investment in the use of SCF_CO₂ for production of fluorinated polymers, see Young and DeSimone (2000). Single-phase solvents are very important in processes where phase separation, and its consequent capillary forces, is

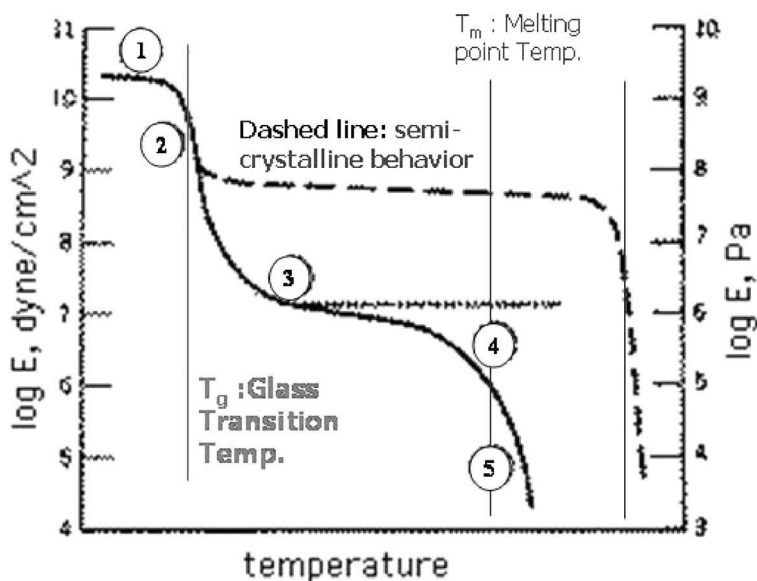


Figure 29. Modulus of elasticity as a function of temperature for polymers. Shows the five regions of viscoelasticity in amorphous polymers, plus the cross-linked behavior, dotted line, and semicrystalline behavior, dashed line.

undesirable such as mass transport within porous media. Although SCFs remain in only one phase in many applications, their remarkable density tunability as a solvent (and hence their solubility) without changes in molecular structure is of great importance.

The important effect of the SCF- CO_2 on polymers is the reduction of the glass transition temperature through sorption and swelling. This effect, also called plasticization, changes the mechanical and physical properties of the polymers. In a sense, the effects of the supercritical CO_2 on polymers are similar to the effects of heating, see Figure 29. Plasticization impacts many polymer processing operations through, (1) viscosity reduction for polymer extrusion and blending, (2) enhancement of diffusion of additives through polymer matrices for impregnation and extraction, (3) enhancement of monomer diffusion for polymer synthesis and foaming, and (4) changes of polymer morphology due to induced crystallization, see Kazarian (2000). Figure 30 shows the effects of supercritical CO_2 on glassy polymers. Implications of the SCF- CO_2 induced plasticization on polymers are discussed at length by Kazarian for the following processes: extraction and drying, impregnation and dyeing, polymer blending, crystallization, foaming of glassy

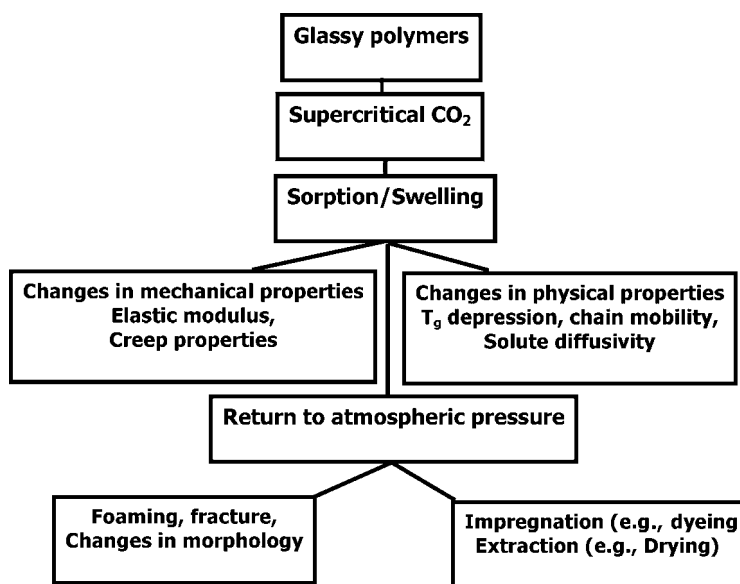


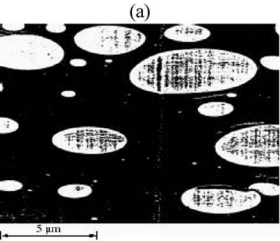
Figure 30. Interaction of glassy polymer with supercritical carbon dioxide.

polymers, and applications in optical materials. Here, a few selected applications are briefly discussed to provide a general awareness of the nature of SCF-CO₂ polymer interaction.

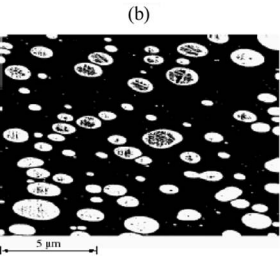
As an application, consider impregnation of polymers by supercritical fluids. It is a process in which high diffusivity, low surface tension/viscosity, and ease of solvent recovery of SCFs are used in order to deposit and/or blend nanoparticles or other solutes to synthesize new polymeric materials. Two approaches are considered for impregnation. First, it involves simple deposition of a substance soluble in the SCF into the polymer matrix. Second, it uses the high affinity of some solutes (in SCF) for certain polymer matrices to achieve preferential partitioning of a solute in favor of a polymer over the fluid, see Kazarian (2000). In one interesting application, a polymer is modified by infusion of a monomer and an initiator into the SCF-CO₂ swollen polymer matrix. The monomer polymerizes in the matrix of the polymer, producing a new blend of polymers with different and improved physical and chemical properties that are difficult to synthesize by conventional methods, see Berens et al. (1986). For example, Elkovitch, et al. (1999) showed the effects of supercritical CO₂ on the blending of PMMA and polystyrene using both a batch mixer (with a single-screw extruder) and a continuous operation mixer (with a twin-screw extruder). Figure 31 shows the effects of SCF-CO₂ on the morphology of the final product. Here, higher solubility of CO₂ in PMMA brings about a greater plasticizing effect leading to the lowering of the viscosity of the PMMA more than polystyrene. Note that the zones of the PMMA have been reduced in size and are more evenly distributed as a result of the addition of the supercritical CO₂ into the system due to the lowered polymer viscosity and possibly influencing the interfacial surface tension between the polymers.

Another exciting application of the supercritical fluid is in the formation of foam materials, see Handa and Zhang (2000). Figure 32 shows the steps that are taken in a typical polymer foaming process and Figure 33 shows sample foam polymers. The first step, is the saturation of a polymer melt with an inert gas, such as supercritical CO₂, under high pressures, followed by a thorough mixing. Thermodynamic instability is then rapidly induced so that numerous vapor nuclei form within the polymer matrix. This can be achieved by either a pressure quench or a sudden temperature increase. The rapid escape of the fluid can cause the nucleation and growth of bubbles within the polymers. The final step of the process is related to the growth of a large number of stable bubble

TEM micrograph of blends of 25/75 PMMA/Polystyrene [Batch mixer]



Without
SCF_CO2



With
SCF_CO2

TEM micrograph of blends of 50/50 PMMA/Polystyrene prepared from twin screw extruder [Continuous mixer]

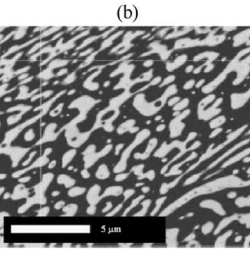
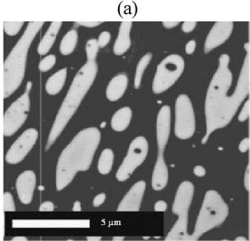


Figure 31. Shows effects blending of two polymers under supercritical CO₂ on the morphology of the product as seen under a transmission electron microscope (TEM). Elkovitch et al. (1999).

nuclei and the subsequent development of a desired microcellular morphology under controlled temperature conditions. Once a significant amount of gas has escaped, the T_g of the polymer drops and “freezes” the foamed structure (anti plasticization).

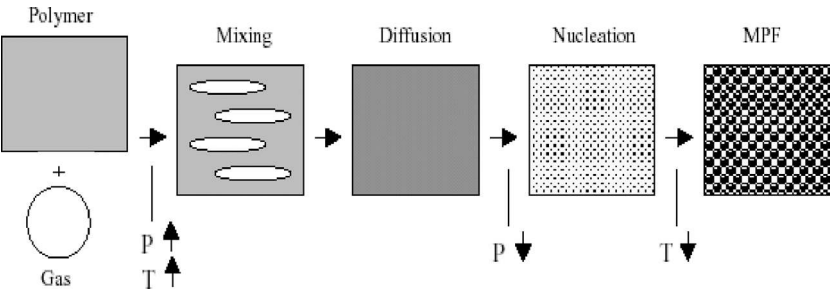


Figure 32. Schematic illustration of the microcellular foaming process. Handa and Zhang (2000).

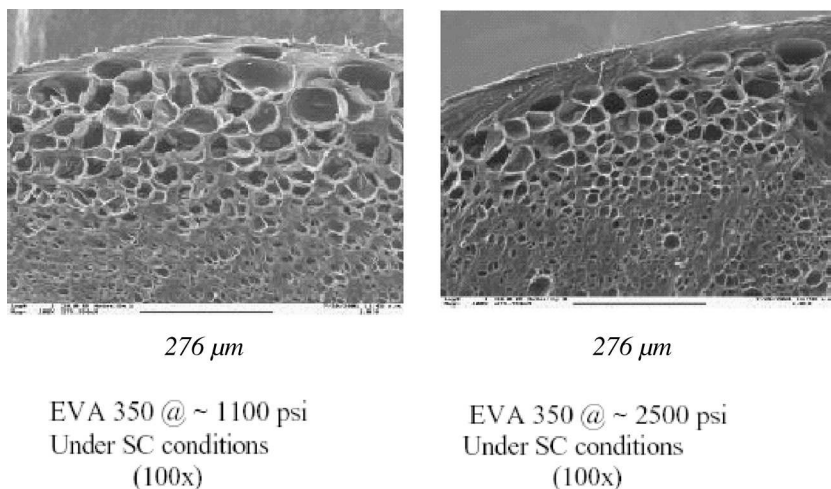


Figure 33. Ethylene Vinyl Acetate (EVA 350) was exposed to supercritical carbon dioxide to alter their properties in this investigation. It was found that the density of these materials varied inversely with the pressure of CO_2 that they were exposed to SC: supercritical condition.

Another application of the plasticizing effect of the supercritical CO_2 is in nonlinear optics components, see Barry and Soane (1996) and Barry and Soane (1991). Azobenzene derivatives are frequently used as dopants in nonlinear optic devices for second harmonic generation. In order to obtain this nonlinear effect, proper orientation of azobenzene chromophores are required. This is usually achieved by “poling” at temperatures near the glass transition temperature of the polymer matrix. However, the reduction of the glass transition temperature via supercritical CO_2 provides an innovative approach to perform the “poling” at room temperature. Figure 34 shows the key idea of the supercritical- CO_2 assisted orientation of nonlinear optical dopants within the polymer matrix by electric field poling at room temperature.

In order to understand some of the processes (such as phase changes during a transitory pressure change) that a polymeric mixture goes through when exposed to $\text{SCF-}\text{CO}_2$, information on its transition states are visualized in Figure 35. This figure shows a general presentation of the pressure-composition (equilibrium) diagram for systems that show liquid-liquid phase separation. The binodal boundary represents the equilibrium demixing pressures for a monodisperse polymer system.

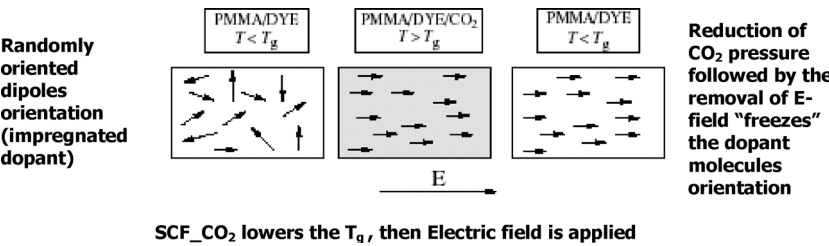


Figure 34. Shows key ideas and steps needed for SCF.CO2 assisted orientation for non-linear optic dopants within a polymer matrix by application of an external electric field. Barry and Soane (1996).

The binodal and spinodal envelopes determine the metastable region (shaded area in the figure). Note that the equilibrium compositions of the two phases when pressure is reduced from P_i to P_f are given by binodals ϕ_{Ib} and ϕ_{IIb} . The solution phase separates into a polymer-lean and polymer-rich phases. The figure is for the equilibrium condition and as

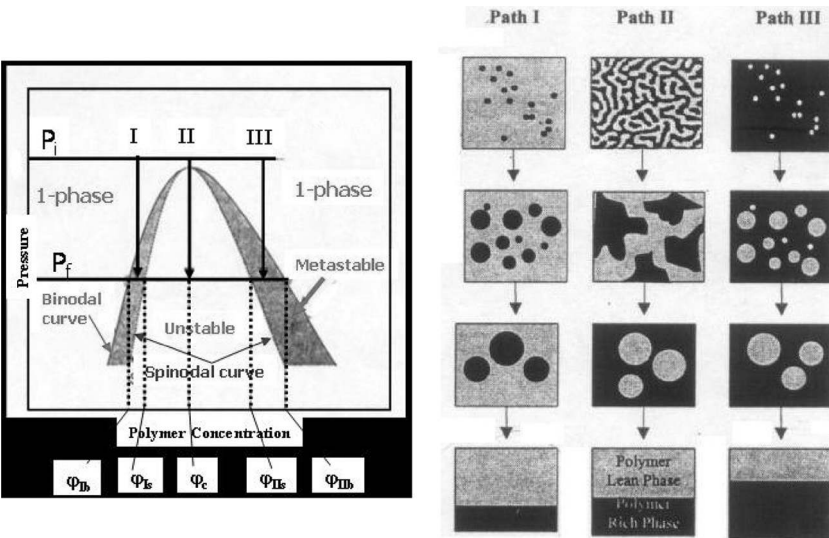


Figure 35. A pressure-composition phase diagram (left), ϕ_{Ib} and ϕ_{IIb} represent the coexistence phase compositions when pressure is reduced from P_i to P_f and the solutions phase separates into a polymer-lean and polymer-rich phase. Transient structure formation and evolution when the nucleation and growth (path I and III) and spinodal decomposition (path II) regimes are entered (right). Kiran and Bayaktar (2000).

such does not describe the transient structure that the system may go through along different pressure quench paths (I, II, III in Figure 34) before reaching its final equilibrium condition. Figure 35 explains the structure of the mixture as it is pressure-quenched via different paths. Along the paths I and III, the system enters into a metastable zone where the mechanism of phase separation is by nucleation and growth. In solutions of low polymer concentrations along the path I, the polymer-rich phase nucleates in the polymer-lean phase, and grows. In contrast, in the more concentrated polymer solutions along the path III, the polymer-lean phase nucleates in the polymer-rich phase and grows. The particles of polymer-rich phase (path I), or the bubbles of polymer-lean phase (path III) unless frozen may eventually collapse, settling into the two coexisting phases with compositions fixed by the binodal values. Path II corresponds to the critical polymer concentration where the system quickly enters the spinodal region where the phase separation is spontaneous, initially forming a continuous texture of polymer-rich and polymer-lean phases, and later the structure becomes coarse and may collapse. For more details see Kiran et al. (2000).

Finally, one interesting application of supercritical- CO_2 in the coating and paint industry is worth mentioning here. Paints used for spray painting technology usually are a mixture of many components such as polymers, pigment, and two different types of solvents. One of them evaporates rapidly and is used to reduce the viscosity of the mixture for better spraying while the other is low in evaporation primarily to dissolve the polymer to promote proper film formation. The fast solvent provides effective atomization of the polymeric material for even coating and evaporates while the droplets are moving towards the target. In this application the fast acting solvent is replaced by the supercritical CO_2 . This new system, named UNICARB, was shown to reduce the harmful volatile organic compounds by about 80%, and improve the finish quality due to improved atomization and spray characteristics, Lee et al. (1991) and Hoy et al. (1993). The mixture starts at high pressures (~ 100 bar) in the one-phase zone and then enters into and passes the liquid-liquid region immediately after passing through the nozzle when the pressure reduces. A further reduction of pressure pushes the system through the three-phase liquid-liquid-vapor line and then ends up in the two-phase liquid-vapor region, see Figure 36. As a result, bubbles of vapor consisting of about 90% CO_2 form and leave the mixture, contributing to the atomization process and raising the viscosity of the

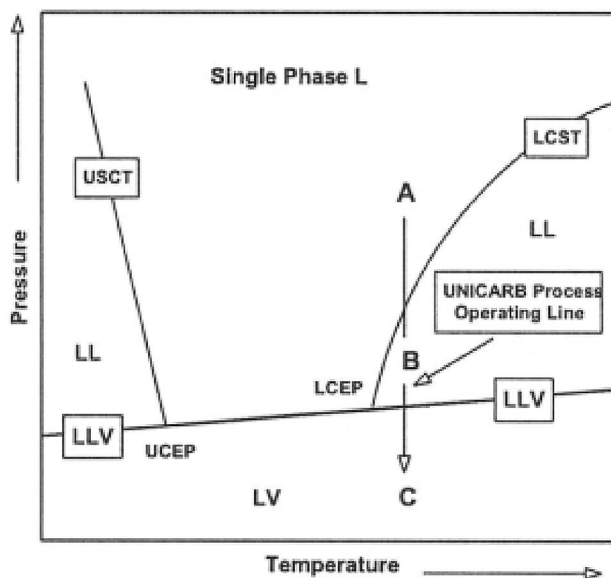


Figure 36. Typical phase diagram of a polymer-solvent- CO_2 mixture. The UNICARB operating line, which runs from point A to B to C is shown. Lee et al. (1991). LLV: liquid-liquid-vapor equilibrium line; UCEP: upper critical endpoint; LCEP: lower critical endpoint. The LCEP and UCEP occur at the intersection of three phase lines with critical mixture curves. At critical end points, two phases critically merge into a single phase in the presence of another phase. UCST: upper critical solution temperature; LCST: lower critical solution temperature.

mixture. Hay (1998) has recently reviewed this spray coating process and it is believed to have advantages over the powder painting approach such as improved film coalescence and quality of the coating.

Other Emerging Applications

There are many emerging applications of the supercritical fluids from which only a few selected ones are presented here. These are judged to be novel, important, and promising by the author. However, for more applications see Darr and Poliakoff (1999), Cansell et al. (2003), Cooper (2001), and Marr and Gamse (2000).

One exciting application of the supercritical CO_2 is in the area of artificial bone synthesis. Howdle et al. (2001) have taken steps in the right direction. As a first step, they found a way to incorporate

hydroxyapatite (calcium phosphate hydroxide) into a biodegradable polymer, poly(lactide-co-glycolide) or PLGA, matrix. Hydroxyapatite is the natural mineralization agent in bone. PLGA is also used in fashioning some drug-delivery devices and as a scaffolding material in tissue engineering. Howdle et al. (2001) took advantage of a method used in powder painting industry under supercritical condition to mix powdered pigments and a polymer, see also Mandle et al. (1998) for details. In this approach the polymer and pigments are mixed in an autoclave which is filled with CO₂ at high pressure. The polymer is plasticized by dissolved CO₂ and the pigment is then homogeneously dispersed in the polymer by way of a stirring device. Rapid depressurization forces a fine-powdered mixture of the polymer and pigment through a nozzle for collection purposes. Note that the entire process takes place at near ambient temperature due to low critical temperature of CO₂. Howdle et al. (2001) were inspired by the process in powder paint industry and used a similar approach to incorporate hydroxyapatite into the PLGA matrix, but modified it by releasing the pressure slowly to make a sponge-like apatite-containing foam. One novel attribute of this method is that it does not use any other solvent and, as mentioned, the whole operation is performed at near room temperature. Howdle's group is now attempting to grow bone tissue by brining both bone-foaming and bone-metabolization cells into hydroxyapatite-loaded PLGA scaffolds.

Howdle et al. (2001) devised a one-step process to produce polymer foams (with controlled pore size) for sustained release of the bioactive compounds. They successfully incorporated different enzymes into the PLGA composite and showed that they maintained their catalytic activities. They stated that the inherently low solubility of the protein in supercritical CO₂ provides a key advantage in preserving protein structure and function. Interestingly, time release of an enzyme over 70 days showed that after an initial burst of about 10% of the drug over the first 2 days, the enzyme was released steadily up to the end. This has very important implications for the pharmaceutical industry. Also, it may have an impact on the design of tissue engineering scaffolds for generating cartilage, bone, and liver tissue.

Another very interesting and promising application at the interface of the nanoworld and supercritical fluid technology is the decoration of nanotubes with nanoparticles of catalysts from its outside under supercritical condition, see Ye et al. (2003). They demonstrated that palladium nanoparticles can be deposited on multi-walled carbon nanotubes

(MWCNTs) by H_2 reduction of $Pd(hfa)_2$ using supercritical CO_2 as a reaction medium ($H_2 + Pd(hfa)_2 \Rightarrow Pd + 2 Hhfa$). It was postulated that due to the high curvature of the MWCNTs, only certain sizes of the Pd nanoparticles can be attached to the outer walls of the MWCNTs. In commercial Pd/Carbon catalyst, activated carbon provides a support to stabilize small Pd particles that are highly reactive. In a sense, the MWCNTs appear to act as a template for decorating nanometer-sized Pd metal particles on carbon surfaces. The MWCNTs were also thought capable of stabilizing nano-sized Pd particles on its external surfaces. Preliminary test showed that the Pd-MWCNT composite exhibits a high catalytic activity for selective hydrogenation of olefins in CO_2 as well as a high electrocatalytic activity for oxygen reduction in potential fuel cell applications. This method can be used to prepare a variety of metal nanoparticles on MWCNTs. The Pd-nanoparticle-MWCNT composite may provide an effective catalyst for chemical synthesis in a green solvent which allows convenient separation of products. For more details see Ye et al. (2003).

SOME FUTURE TRENDS IN NANOTECHNOLOGY

The future appears bright and promising for the nano-related science and technology as far as its penetration into a wide range of other "old" technologies is concerned. The material science applications of nanotechnology continue to lead the expansion for the foreseeable future. Next, the microelectronic industry has keen interest in pushing the limit of lithography and has already entered into the world of the nanostructured materials and manufacturing. It is clear that the growth in commercialization will be mostly seen in these areas. One important growth area is in the instrumentation required for the visualization of the nanosized structures. Before being able to harness the promising features of this new technology, researchers must possess convenient tools to not only "see" but manipulate the building block within the nanolandscape. Hence, one of the areas with potential growth is projected to be at the interface of the virtual reality and atomic force microscopy (AFM). This is expected to tremendously facilitate research activities. It is important to indicate that the historical growth in the science of virology has only accelerated when electron microscope became commercially available for the researchers to see the viruses and understand their interactions with other biological species. The so-called "bottom-up" approach or self-assembly of the building blocks in the nanoworld

appears to be an area of exponential growth. For example, nearly half of the 994-page Proceedings of the National Academy of Sciences in April 16, 2002 is devoted to supramolecular chemistry and self-assembly. Due to the natural overlap between the nanoworld and biological arena, tremendous expansion is expected in a number of applications such as new cancer fighting methods, drug delivery, and nano-biodevices. For example, in nanofluidic chips, tiny channels (50 nm) on the silicon chip squeeze and barely allow passage of a single strand of labeled DNA through the device (a key feature of the device). As DNA passes down the nanochannel, an optical detector identifies the genetic labels. Also, IBM has introduced nanocantilever beams in what is called a protein analysis chip. Finally, due to the highly multidisciplinary nature of this present revolution in science and technology, educational institutions are beginning to feel the need for courses in nanotechnology. In light of the fundamental nature of the field, specialized multidisciplinary degrees (MS or PhD) are needed. Truly multidisciplinary centers are being formed throughout the world, for example, the MESA + Research Institute in the Netherlands.

FUTURE OF SUPERCRITICAL FLUIDS IN NANOTECHNOLOGY AND OTHER EMERGING AREAS

As a solvent, supercritical fluids show great potential for manufacturing of nanostructure materials. At the nano scale, as realized for years in the field of aerogels, high surface tensions and appreciable capillary forces can be very destructive. Hence, considering that SCFs could eliminate surface tension and capillary forces, only this one attribute of the SCFs is sufficient to define a large overlap between the two disciplines. Also, in chemistry, supramolecular constructs are usually formed in solutions, and self-assembly processes are undoubtedly influenced by solvent properties such as density, dielectric constant, and polarizability. Most of these variables can be fine-tuned in compressible SCF solvents. This area, molecular self-assembly, will most likely be one of the frontiers of nanotechnology in which SCFs could play a key role.

SUMMARY AND CONCLUSIONS

Nanotechnology is likely to have a revolutionary impact on a number of key technologies in a not too distant future. In particular, production of

nanoparticles (using SCFs) as a building block in the nanoworld is one central theme of this technology. The growth of nanotechnology to a large extent depends on how the key tools to manipulate, "see," and fabricate the nanoworld develop (both technologically and commercially). Reduction of acquisition costs and their availability will largely determine the growth time scale in many areas.

Supercritical fluids offer an important opportunity for exciting research with a good potential for harnessing the results in industrially important processes for sustainable growth in the new millennium. It is seen that the solubility of supercritical fluids decreases with decreases in density (i.e., with decreasing pressure). This aspect is employed in many applications such as rapid expansion of supercritical solutions, leading to the precipitation of finely divided solids (nanoparticles). SCFs also offer multidisciplinary research and commercialization opportunities for purifying proteins, producing micro- and nanoparticles via rapid expansion and antisolvent precipitation, creating protein powder, preparing liposomes encapsulating water-soluble compounds, and aerosol production for fine powder generation and nano-drug delivery.

The high solubility of fluorinated block copolymers in supercritical CO_2 and the selectivity of supercritical CO_2 to, both, polarity changes and the molecular structure of the polymer were used to develop an environmentally friendly lithographic process. This method could be superior to that of aqueous-based nongreen approaches practiced today. Phase elimination and zero surface tension of the SCFs are important properties that enable them as a fluid of the choice in cleaning applications, especially when nanosized crevices and features sizes are involved. This key characteristic of SCFs creates an important intrinsic overlap between the supercritical technology and nanotechnology.

SCFs have solvent powers similar to light liquid hydrocarbons for most solutes. However, fluorinated compounds are often more soluble in supercritical CO_2 than in liquid hydrocarbons. This increased solubility is important for their polymerization. Clearly, supercritical CO_2 may be used in polymer-ceramic composites to influence the processing rheology of these compounds, as well as their supercritical fluid extraction and drying. In general, SCFs will play an increasingly important role in the manufacturing of high-value-added materials for a broad range of applications.

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APPENDIX

Surface Plasmon

Conduction electrons (–) and ionic cores (+) in a metal form a plasma state. When external electric fields (electro-magnetic waves, electron beams etc.) are applied to a metal, electrons move so as to screen perturbed charge distribution, further move beyond the neutral states, and

again return to the neutral states and so on. This collective motion of electrons is called a “plasma oscillation.” The surface plasmon resonance is a collective excitation mode of the plasma localized near the surface. Electrons confined in a nanoparticle conform the surface plasmon mode. The resonance frequency of the surface plasmon is different from an ordinary plasma frequency. The surface-plasmon mode arises from the electron confinement in the nanoparticle. Since the dielectric function tends to become continuous at the interface (surface), the oscillation mode shifts from the ordinary plasma resonance and exponentially decays along the depth from the surface.